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Professor Ordinarius in the University of Amsterdam, Netherlands,

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A TEXT-BOOK

OF

INORGANIC CHEMISTRY.

BY

DR. A. F. HOLLEMAN,
Professor Ordinarius in the University of Amsterdam; Emeritus Professor Ordinarius in the University of Groningen, Netherlands, and Fellow of the Royal Academy of Sciences, Amsterdam.

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PREFACE TO THE THIRD EDITION.

THE present edition represents a thorough revision of the work by both the Dutch author and the American editor. The portions on the phase rule, spectroscopy, radio-activity, iron-carbon system and metal-ammonia compounds have been largely rewritten by the author, and the chapter on colloids, experimental determination of equivalent weights and unity of matter, are entirely new. Professor WERNER has kindly approved the chapter on metal-ammonia compounds.

Professor HOLLEMAN'S unusual ability as a text-book writer seems to exhibit itself not only in the lucid presentation of chemical facts and their generalizations, but also in a cosmopolitan point of view. The American edition is independent of all editions of the work in other languages, so far as the American editor is concerned, but it profits from the author's experience with the foreign editions.

Notwithstanding the appearance of differential formulæ in the book, it is believed that a student who is unfamiliar with the calculus should have little difficulty in understanding the meaning and use of such formulæ, provided he is willing to take the author's word for the solutions of the equations.

References in the text to "Organic Chemistry" refer to the companion volume of this work, HOLLEMAN'S "Text-book of Organic Chemistry," translated by WALKER and MOTT.

H. C. COOPER.

SYRACUSE UNIVERSITY,
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INORGANIC CHEMISTRY.

INTRODUCTION.

1. **Chemistry** is a branch of the natural sciences,—the sciences which deal with the things on the earth and in the outside universe. The knowledge of these things is obtained by observation with our senses, this being the only means we possess. It is well to understand, therefore, that we know not the things themselves, but simply the impressions which they make upon our sense-organs. When we see an object, we perceive, in reality, only the effect on our retina; if we feel the object, it is not the body itself but the excitement of the sensory nerves of touch in our fingers that we are made aware of. Hence it may be fairly asked whether the objects of which we are cognizant are really just as we perceive them, or whether they even exist at all outside of our person. The natural sciences leave this problem out of consideration—its solution is the task of speculative philosophy. In reality they are not concerned with the objects, which in themselves we cannot know, but with the study of the sensations that we receive. The sensations take the place of the objects, and we regard them as such.

2. **The Scientific Investigation of Things.**—What is to be understood by the term? In the first place, a most accurate *description* of the objects. From a study of this it is found that many objects resemble each other to a greater or less degree, and it is therefore possible to make a classification, i.e. an arrangement of like objects into groups and a separation of the various groups from each other. By the descriptive method we are finally able to divide the natural sciences into *Zoology*, *Botany*, *Mineralogy* and *Astronomy*.

3. In the second place, scientific investigation includes the

study of the relations which the objects bear to each other; in other words, the study of *phenomena*. The heavenly bodies move towards each other; water turns to ice on cooling; wood burns when heated. It is the task of the natural sciences to accurately observe and describe such phenomena, i.e. to ascertain in what way the heavenly bodies change their relative positions, what conditions affect the freezing of water, what becomes of the burning wood, under what conditions it can burn, etc.

The description of the phenomena leads to a different division of the natural sciences than the description of objects, viz., a division into *Physics*, *Chemistry* and *Biology*, the latter being the study of vital processes, and including Physiology, Pathology and Therapeutics.

4. The human mind, in pursuing the scientific study of nature, does not feel contented with the accurate description of objects and phenomena; it seeks also for an *explanation* of the latter. The various attempts at explanations constitute the most important part of science. When, for instance, we see that a ray of light in passing through a piece of Iceland spar is split up into two other rays of different properties, we strive to account for tho phenomenon. When copper is heated in the air, it turns into a black powder; the question again arises, why this thing is so. In searching for an explanation of the phenomena we thus endeavor to penetrate deeper into the essence of things than is possible by direct observation. Although the phenomena themselves are found to be unchangeable, our explanation of them may be modified as our knowledge increases. The transformation of copper into a black powder on heating in the air was formerly explained by the supposition that something left the metal; subsequently, when the phenomenon was better understood, by assuming that the copper takes up something from the air.

Scientific investigation pursues in general, then, the following course: A phenomenon is observed and studied as carefully as possible. Thereupon an explanation of it is sought. A **hypothesis** is set up. From this conclusions can be formed, some of which can be tested by experiment. If the latter really leads to the expected result, the hypothesis gains in probability. If it is subsequently found to explain and link together a whole series of phenomena, it becomes a **theory**.

The nineteenth century was an era of great prosperity for scientific inquiry. For numerous phenomena explanations have been found which possess a great degree of probability. Still it cannot be denied that the present theories penetrate only a little into the real essence of things, and the investigator very soon stumbles upon questions whose explanation does not at present even seem to be a possibility. The chemical process that goes on when copper—to retain our former example—is heated in the air is well known. However, the deeper question, why the action takes place just so and not otherwise, or why the resulting powder is black, still awaits a satisfactory answer.

5. We observed in the preceding paragraph that the natural phenomena are found to be unchangeable. The movement of the planets, for example, still takes place in the same manner as in the times of the Ptolemies; whenever water turns to ice the same increase of volume is to be observed; the crystal form of common salt, whenever and wherever examined, is invariably the same; from the burning of wood the same products are always obtained; the microscopic structure of the leaves of one and the same plant is never found to vary. This general principle finds its expression in the phrase, *constancy of natural phenomena.* Every one is convinced of its truth, and it is tacitly accepted as the basis of every natural scientific investigation. If, for example, one has measured the angles which the faces of a soda crystal form with each other, he considers it certain that all soda crystals must show the same angles, at whatever time or place they may be measured. If it has once been determined that pure alcohol boils at 78° under normal pressure, it is forthwith assumed that this must be the case with all alcohol, no matter how it may be obtained or when and where it may be tested.

PHYSICAL AND CHEMICAL PHENOMENA.

6. It was stated above (§ 3) that the description of phenomena leads to a division of the natural sciences into Physics, Chemistry and the study of vital processes (Biology). In defining the province of Chemistry Biology may be left out of consideration; however, it is desirable to compare the field of Chemistry with that of Physics. In general it may be said that Physics deals with the

temporary, Chemistry with the lasting, changes of matter. By *matter* or *substance* we understand the objects without reference to their form. Iron, marble, sand and glass are kinds of matter, or *substances*, independent of their external shape.

A couple of illustrations may make this conception of temporary and lasting changes clear.

(*a*) A platinum wire glows when held in a colorless gas-flame. On removal it cools off and no change is visible. This is a physical phenomenon; the change, the glowing, is of a temporary sort. So soon as the cause of the change is removed, the wire resumes its original condition. When some magnesium wire is held in the flame, it burns with the emission of a brilliant light and turns into a white powder, which is wholly different from the substance magnesium. Here a lasting change has occurred; we have to do with a chemical phenomenon.

(*b*) Again, we may take two white crystallized substances, naphthalene and cane-sugar, and heat each separately in a retort with receiver. The naphthalene at first melts; on continued heating it begins to boil, then distils over and condenses in the receiver. The distilled naphthalene resembles the undistilled in every respect. The substance has, as a result of heating, undergone physical changes—melting, change to vapor and, finally, return to the solid state. The cane-sugar behaves differently. Here also a melting is observed at first, but soon the sugar turns darker; a brownish liquid distils over; a peculiar odor is noticeable and at last there remains in the retort a charred, porous mass. The cane-sugar suffers a lasting change on being heated. In this case we have a chemical change.

(*c*) As a third and last example we may consider the behavior of a metallic wire on the one hand and that of acidulated water on the other, when an electric current passes through them. The wire displays other properties so long as the current is on. If the latter ceases, the wire returns to its original condition. This is a physical action. In the acidulated water, however, the current induces an evolution of gas, and this gas arising from the water has properties entirely different from those of the water. A lasting change in the substance has occurred; a chemical action has taken place.

A *sharp* distinction between physical and chemical phenomena is often—as will be seen later—very difficult to make.

CHEMICAL OPERATIONS.

7. In order to avoid repetitions it seems advisable at this point to describe briefly some of the commonest chemical operations.

Solution.—When sugar, salt or saltpetre, for example, is put into water, the solid substance disappears and its taste is taken on by the water. The substance has *dissolved* in the water. There is a definite limit to the solubility of each of these, for, if the temperature is kept constant and more of the substance is gradually added, a point is finally reached when the water will take up no more. The solution is then *saturated.* The solubility of most solids increases with the temperature. Moreover it is very different with different substances, varying all the way from solubility in all proportions to imperceptible solubility. Thus cane-sugar is dissolved in large quantity by water, while sand is practically insoluble in it. Liquids can be either miscible in all proportions (water and alcohol) or only partially soluble in each other. When, for instance, water is shaken with a sufficient quantity of ether and allowed to stand, two liquid layers are formed; the water has dissolved some ether and the ether some water. In most cases the solubility of liquids in each other also increases with the temperature. In the case of gases solubility decreases with rising temperature.

Separation of a Solid and a Liquid.—This may be accomplished by **filtration.** A funnel is lined on the interior with "filter-paper" and the mixture poured upon it. The solid is retained on the paper while the liquid passes through. **Decantation** is a less complete method of separation, since more liquid remains with the solid by this method than by filtration. However, it is evident that neither method affords a really complete separation. This can only be accomplished by washing, i.e. by replacing the portion of the liquid which remains between the solid particles by another liquid. If the liquid of the mixture be a salt solution, pure water is very effective. It is obvious that by repeating the washing several times the salt solution can be wholly removed. Suppose that 1 c.c. salt solution remains between the particles of the solid and that 9 c.c. water is then added. The solution is thus reduced to one-tenth of its original concentration. If 1 c.c. of this dilute solution again remains with the solid and another

9 c.c. water is added, the concentration is then 10^{-2}, or one-hundredth of the original concentration; after six such operations it would be only 10^{-6}, or one millionth of the original, so that the separation is practically complete.

Crystallization.—If a solution is saturated in the warm and is then allowed to cool, the dissolved substance frequently separates out in the crystallized state. Advantage is often taken of this for purifying crystallizable substances.

Distillation (Fig. 1).—This operation is frequently made use of in working with liquids. The liquid is placed in a flask or a retort and heated to boiling. The escaping vapor is cooled to a liquid in a *condenser*. The latter consists of a sufficiently wide tube encased in a jacket, through which water flows to keep the inner tube cold. The condensed liquid is collected in the *receiver*.

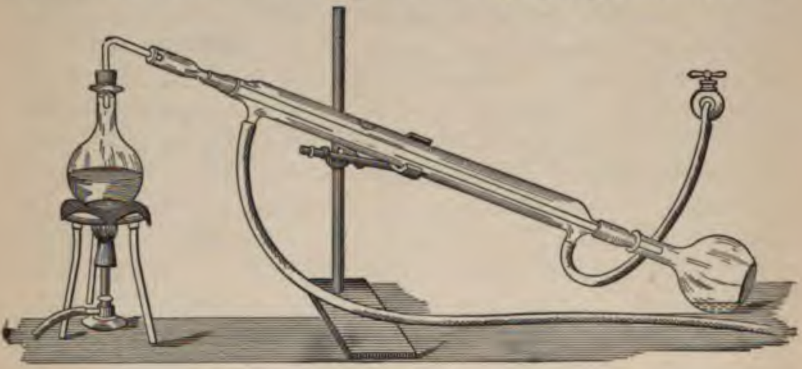

FIG. 1.—DISTILLATION.

It is readily seen how volatile substances can be separated from non-volatile ones by distillation, e.g. water from salt, since the former distil over and the latter remain in the distilling-flask. However, liquids of different volatility can also be separated in this manner. Take, for example, a mixture of alcohol and water. The more volatile constituent, alcohol, passes over for the most part in the early stage of the operation; towards the end the less volatile, water. If the two distillates are collected separately, an approximate separation results. A few repetitions of this so-called *fractional* distillation bring about a practically complete separation in many cases.

Sublimation.—Certain solids, e.g. camphor, when heated (at ordinary pressure), turn to vapor without melting. If this vapor comes in contact with a cold surface, the substance is deposited in the solid, crystallized state. It is evident that we have here another method of separating some substances.

THE ELEMENTS.

8. When a substance (§ 6) is subjected to various influences, such as heat, electricity, or light, or is brought in contact with other substances, it is very often split up into two or more dissimilar components. As an example let us take gunpowder. Water is added and the whole is stirred well and gently warmed; after a while it is filtered, and that which remains on the filter is found to be no longer gunpowder, for it is unexplosive. On evaporating the filtrate a white crystalline substance, saltpetre, remains. The undissolved part is dried and then shaken with another solvent, carbon disulphide. After a time the mixture is filtered, as before, and there is left on the filter a black mass, consisting of charcoal powder. The carbon disulphide of the filtrate evaporates and leaves yellow crystals of sulphur. Thus we see that, by successive treatment with water and carbon disulphide, gunpowder can be separated into three substances, viz. carbon, sulphur and saltpetre. The two former are incapable, even when subjected to all the agencies at our command, of division into different components. Not so with saltpetre, for when the latter is heated strongly a gas is given off in which a glowing wooden splinter is at once ignited. When the evolution of gas ceases, a substance remains which gives off red fumes on treatment with sulphuric acid, something that saltpetre does not do. Saltpetre can evidently be broken up still farther by heating.

If we subject all sorts of substances to a successive treatment with reagents of the most different kinds, we finally discover certain ones that cannot be resolved into simpler substances by our present means. Such substances are called **elements.** Although the number of substances, according to § 6, may be considered as infinitely great, experience has taught that the number of elements is small. There are about *seventy*.

As our methods of examination improve, it may quite possibly be found that the substances which the chemist of to-day regards as elements have no right to the name. Therefore, when we use the word "element," it is to be regarded as a relative term, dependent on the extent of our knowledge and the means at our command. In the history of chemistry some cases are to be found where substances, once believed to be elements, were subsequently decomposed.

The exact number of elements cannot be definitely stated, because, on the one hand, not all the substances that possibly exist may be within our reach,* and, on the other hand, it is doubtful whether certain substances now regarded as elements cannot be divided by means already known.

The following is an alphabetical list of the elements at present known to exist:

Aluminium
Antimony
Argon
Arsenic
Barium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Cæsium
Calcium
Carbon
Cerium
Chlorine
Chromium
Cobalt
Copper
Dysprosium
Erbium
Fluorine
Gadolinium
Gallium
Germanium
Gold
Helium
Hydrogen
Indium
Iodine
Iridium
Iron
Krypton
Lanthanum
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Neodymium
Neon
Nickel
Niobium
Nitrogen
Osmium
Oxygen
Palladium
Phosphorus
Platinum
Potassium
Praseodymium
Radium
Rhodium
Rubidium
Ruthenium
Samarium
Scandium
Selenium
Silicon
Silver
Sodium
Strontium
Sulphur
Tantalum
Tellurium
Terbium
Thallium
Thorium
Thulium
Tin
Titanium
Tungsten
Uranium
Vanadium
Xenon
Ytterbium
Yttrium
Zinc
Zirconium

As may be seen from this list, the *metals* are included in the elements. Together with them we find a number of other substances, as oxygen, sulphur, phosphorus, etc., that are classed under the term *non-metals*, or *metalloids*. To the latter class belong many very important substances, e.g., oxygen, an element that combines with almost all others, causing what is called combustion. Oxygen is present in a large amount in the air. Another non-metal is carbon, which is present in all organized substances, and is therefore a constituent of every animal and plant. Sulphur, which burns with a blue flame, giving off a pungent odor, and chlorine, a greenish-yellow gas of very disagreeable odor, which combines readily with most metals, are also non-metals.

---

* Of the interior of the earth only a very small part is known. If we think of the earth as about the size of an orange, the deepest mine-shafts would not even penetrate the thin yellow exterior layer of the orange-skin.

The elements occur in very unequal proportions in the part of the earth accessible to us. Oxygen, which occurs in air, in water, and in the solid part of the earth's crust, is very preponderant, composing approximately 50% of these portions of the earth which have been investigated. The elements silicon, aluminium, iron, calcium, carbon, magnesium, sodium, potassium, and hydrogen, together with oxygen, make up 99% of the earth's crust. There remains, therefore, only 1% for all the other elements. Some of these are quite common, e.g., lithium, but they almost always occur in very small quantities. Others, like niobium and tantalum, are found in relatively very small amounts and in isolated places.

The following table, according to CLARKE, gives an approximate summary of the quantities of the elements found in the part of the earth accessible to us:

	Earth's Crust. 10 miles downward (93 per cent).	Ocean. (7 per cent).	Atmosphere.	Average.
	%	%	%	%
Oxygen	47.07	85.79	23.02	49.78
Silicon	27.06	.....	.....	26.08
Aluminium	7.90	.....	.....	7.34
Iron	4.43	.....	.....	4.11
Calcium	3.44	0.05	.....	3.19
Magnesium	2.40	0.14	.....	2.24
Sodium	2.43	1.14	.....	2.33
Potassium	2.45	0.04	.....	2.28
Hydrogen	0.22	10.67	.....	0.95
Titanium	0.40	.....	.....	0.37
Carbon	0.20	0.002	.....	0.19
Chlorine	0.07	2.07	.....	0.21
Bromine	.....	0.008		
Phosphorus	0.11	.....	.....	0.11
Sulphur	0.11	0.09	.....	0.11
Barium	0.09	.....	.....	0.09
Manganese	0.07	.....	.....	0.07
Strontium	0.03	.....	.....	0.03
Nitrogen	.....	.....	75.54	0.02
Fluorine	0.02	.....	.....	0.02
All other elements	0.50	.....	1.44	0.48
	100.00	100.00	100.00	100.00

With the aid of spectrum analysis (§§ 263–267) it has been ascertained that the heavenly bodies contain most of the elements found in our earth, and also some others.

OXYGEN.

9. Under ordinary conditions of temperature and pressure, oxygen is a colorless and odorless gas, whose most noticeable property is its ability to set glowing substances on fire with the evolution of much light and heat. A glowing splinter of wood, for example, when introduced into an atmosphere of oxygen, begins at once to burn brightly. This action is ordinarily used as a *characteristic test* for the identification of oxygen.

This gas can be obtained in various ways. There are many substances which are known to evolve oxygen on heating.

(1) *Mercuric oxide*, when heated strongly in a retort (Fig. 2), yields oxygen, which can be collected by means of a delivery-tube opening under the mouth of a cylindrical receiver filled with water. The inside of the retort becomes covered with drops of mercury.

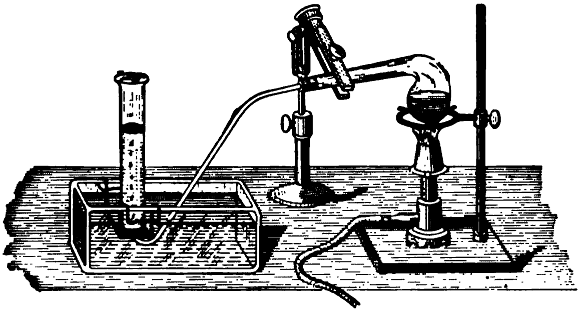

FIG. 2.—PREPARATION OF OXYGEN FROM POTASSIUM CHLORATE.

(2) The same apparatus can be used in making oxygen from *potassium chlorate* (chlorate of potash), as well as from *potassium nitrate* (saltpetre), *potassium permanganate*, and many other substances. The preparation of oxygen by heating potassium chlorate is a method frequently used in the laboratory.

Some substances give off oxygen when heated together with others, as in the following cases:

(3) Potassium dichromate or manganese dioxide, when heated with sulphuric acid;

(4) Zinc oxide, when heated in a current of chlorine.

The atmospheric air consists principally of oxygen and nitrogen. The following method for separating these gases was employed by **Lavoisier** in 1774. He introduced some mercury into a retort *A* (Fig. 3) with a long, doubly-bent neck that opened under a bell-jar *P* filled with air and resting in a dish *R* of mercury. He then heated the retort steadily for several days, keeping the mercury almost boiling. As a result, a part of the air in *P* disappeared, and the gas remaining was found to possess other properties than air—it was nitrogen. At the same time the mercury had been partially transformed into a red powder, mercuric oxide. On heating the latter more strongly oxygen was obtained.

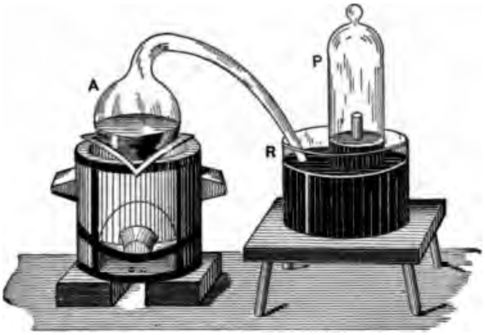

Fig. 3.—Absorption of Oxygen by Mercury.

Oxygen is manufactured on a large scale commercially by the **Kassner** process (*cf.* § 204).

The *physical properties* of oxygen, besides those already mentioned, are as follows: Its specific gravity, assuming the density of air to be 1, is 1.10535; taking hydrogen as unity, it is 15.88. A liter of oxygen at 0° and 760 mm. Hg pressure weighs 1.4290 g. Oxygen can be liquefied; the difficulties in obtaining it on a large scale in the liquid state have now been completely overcome. Apparatuses for liquefying oxygen have been constructed by **Hampson** and by **Linde**, a description of which is to be found in text-books of physics. The critical temperature of oxygen is $-118°$, and its critical pressure 50 atmospheres. Liquid oxygen has a specific gravity of 1.124 (based on water) and a boiling-point of $-182.95°$ at 745.0 mm. pressure. Its color is light blue. It can be preserved for some time at ordinary pressure, with the aid of a so-called vacuum-flask (Fig. 4.) The latter is a vessel enclosed in an air-tight jacket, the space between the walls being evacuated. 100 l. water at 0° dissolves 4.89 l. oxygen. The gas is also somewhat soluble in alcohol and in molten silver. When the silver solidifies, the oxygen—a volume about ten times that of the metal—suddenly escapes from solution, causing peculiar elevations on the surface of the silver ("spitting" of silver).

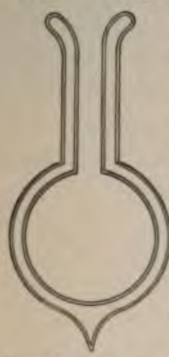

FIG. 4.—VACUUM-FLASK.

We remarked above (§ 7) that the solubility of gases in liquids diminishes with increasing temperature. A very remarkable law expresses the relation that exists between the solubility of a gas and its pressure, namely, *the solubility is proportional to the pressure.* This is the *law of* HENRY. Thus, when the pressure becomes a-fold, the solubility also becomes a-fold. As the mass of a gas which is present in a certain volume is likewise proportional to the pressure, the law of HENRY can also be expressed thus: *The volume of a gas dissolving in a certain quantity of a liquid is independent of the pressure.*

This law is rigid when the solubility of the gas is small; when the solubility is large, for instance 100 volumes in 1 of the liquid, its deviations are considerable.

Still another formulation of this law is of value in understanding certain of its applications: *The concentrations of the dissolved and undissolved portions of a gas bear a constant ratio to each other.* By "concentration" is meant the quantity of the gas in grams per unit volume (cubic centimeter).

10. Among the *chemical properties* of oxygen the most prominent is its vigorous support of combustion. The following are interesting examples:

Charcoal glows in air only moderately and without much evolution of light. In oxygen, however, it burns with a bright glow. Sulphur, which burns in air with only a small flame, burns in oxygen with an intense blue light. Phosphorus burns in oxygen with a blinding white light. A steel watch-spring that has been heated to redness at one end and put into oxygen, burns with scintillation. Zinc also burns in it with a dazzling light. In all these and analogous cases the oxygen, as well as the burning material, disappears during the combustion, while new substances are formed. A lasting change therefore takes place and we have to do with a chemical process. The product of burning charcoal is found to be a gas that makes lime-water cloudy and is unable to support combustion; it is called carbonic acid gas. Sulphur also yields a gas; it has a pungent odor and is called sulphur dioxide. Phosphorus produces a white flocculent powder, phosphorus pentoxide. When iron burns, a black cindery powder is formed, called "hammer-scale," because it composes the sparks that fly from the anvil.

The question now arises as to what really occurs in the above cases. In the first place, it has been found that the weight of the product of combustion is greater than that of the substance burned.

The increase in weight of the substance during burning can in many cases be easily demonstrated. For instance, a horseshoe magnet that has been dipped in iron filings may be hung on the lower side of a scale-pan and balanced by weights put in the other pan. The iron filings may be burned by passing a non-luminous flame under them a few times. On cooling, the scale-pan attached to the magnet sinks. In a similar way one may demonstrate the increase of weight in the burning of copper. In order to prove the increase of weight in a case where only gaseous products are formed, a candle may be burned and the combustion products, carbon dioxide and water vapor, collected by letting them pass over unslaked lime, with which both unite.

Closer investigation has revealed the fact that the increased weight is due to the presence of oxygen, as well as the burned substance, in all combustion products. The latter are *compounds* of these substances with oxygen. The participation of oxygen in the burning of zinc, for example, may be proved by heating the combustion product, zinc white, in a tube and leading over it chlorine gas, whereby oxygen is driven off. The compounds of oxygen are called **oxides,** and the act of this combination is known as **oxidation.**

When substances burn in the air, it is only the oxygen which combines with them. Nevertheless, the nitrogen of the air is heated and thus takes a part of the heat evolved in the combustion.

Therefore the temperature of a burning object cannot rise so high as in pure oxygen, and, since the emission of light increases very rapidly as the temperature rises, combustions in oxygen are for this reason much brighter than in air.

There are two general methods of ascertaining what elements exist in a compound. According to the one method the compound is decomposed and the elements composing it thereupon determined. This is the *analytic* method. According to the other, the *synthetic* method, the composition is found by combining different elements to form new substances. In the above-described experiment (§ 8) of LAVOISIER the composition of the red powder is learned by decomposing it at high temperature, whereupon it separates into only mercury and oxygen. Inversely it was possible to obtain the red powder by heating pure oxygen and pure mercury together at a lower temperature. The former is an example of analysis, the latter of synthesis.

HYDROGEN.

11. Hydrogen is a colorless and odorless gas that is rarely found on the earth in the free state. The gases of some volcanoes contain it and it can also result from processes of decay. In combination with other elements, however, hydrogen is very widely distributed and occurs in very large amounts (§ 8).

Hydrogen can be prepared in various ways. In the first place, hydrogen compounds can be broken up.

(1) Water is decomposed by the electric current, hydrogen being evolved at the negative pole (cathode).

(2) Palladium-hydrogen is broken up by heat into palladium and hydrogen (see § 315).

The ordinary methods of preparing hydrogen depend on the indirect decomposition of hydrogen compounds, i.e. their reaction with other substances. The following are examples of this sort:

(3) The action of zinc on dilute sulphuric acid (§ 89). This is the ordinary method.

For the preparation of hydrogen in the laboratory the apparatus shown in Fig. 5 is often used. *A* contains granulated zinc (or iron nails) and *B* dilute hydrochloric acid or sulphuric acid. When the cock *C* is opened the acid flows through *D* to the metal and the evolution of hydrogen commences at once. The cock being closed again, the gas still continues to come off and forces back the acid. This is facilitated by changing the relative levels of *A* and *B*.

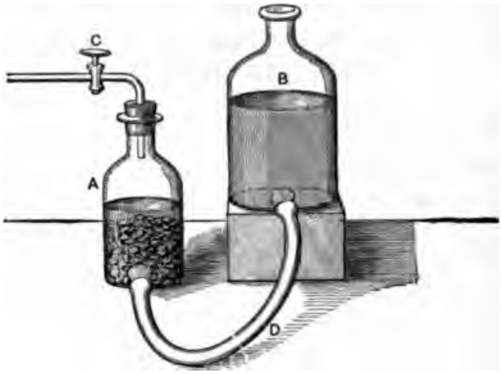

FIG. 5.

(4) The action of zinc or aluminium filings on caustic potash or slaked lime.

(5) The action of sodium or potassium on water or alcohol.

(6) Magnesium powder, when boiled with water, also evolves hydrogen, especially when some chloride of magnesium is dissolved in the water, because such a solution dissolves the magnesium oxide which forms on the surface of the metal. Likewise, red-hot iron decomposes water with the liberation of hydrogen (compare § 305).

12. The *physical properties* of hydrogen are these: It is the lightest of all known substances, its specific gravity (air = 1) amounting to only 0.06949. One liter of hydrogen at 0° and 760 mm. Hg. pressure weighs 0.0899 g. Its lightness renders it useful for inflating balloons. It is very hard to liquefy, because its critical temperature lies only 30–32° above the absolute zero (−273°). On the other hand, the critical pressure is only 15 atmospheres. Liquid hydrogen is colorless. It boils at −252.5°. Its specific gravity, with reference to water, is only 0.07 at its boiling-point and 0.086 at its freezing-point, being therefore considerably less than that of all other known liquids. DEWAR further succeeded in bringing hydrogen to the solid state by allowing the liquid to evaporate quickly at 30–40 mm. pressure. The melting-point of solid hydrogen is about 16° (absolute temperature). The heat of evaporation of liquid hydrogen is very high, being 200 cal.; for this reason a flask containing liquid hydrogen soon becomes covered with a layer of liquid air, which drops down and soon partially solidifies.

Hydrogen is slightly soluble in water, 100 l. water dissolving 2.15 l. of the gas at 0°. Alcohol takes up somewhat more.

13. *Chemical Properties.*—Hydrogen does not unite with as large a number of elements as oxygen. At a higher temperature it displays a strong tendency to unite with oxygen, burning with an almost colorless and a very hot flame to form water. This property serves for the identification of hydrogen gas.

When a current of hydrogen is directed upon very finely divided platinum (spongy platinum or platinum black, § 316), the hydrogen is ignited (§ 25).

The high temperature of the hydrogen flame is made use of in fusing platinum, quartz, etc., and in the *Drummond lime-light.*

In the latter oxygen is forced into a hydrogen flame, which is directed on to a piece of quicklime. The intense heat causes the latter to glow brilliantly.

Such a flame is known as an oxyhydrogen flame. An apparatus (*oxyhydrogen blowpipe*) like that represented in Fig. 6 is required for producing it. The hydrogen enters at *W* and passes out at *a*, where it is lit. Oxygen is blown into the flame at *S*. Thus the gases do not mix till they reach the flame, and the possibility of an explosion is avoided.

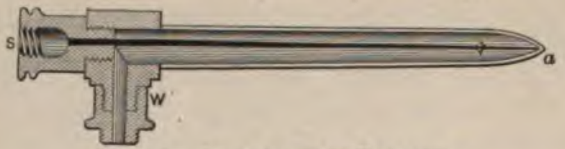

FIG. 6.—OXYHYDROGEN BLOWPIPE.

A mixture of hydrogen and oxygen, especially in the proportion of 2 vols. H and 1 vol. O (*detonating-gas*), when ignited, turns instantaneously to steam; in other words, it explodes. This experiment can, however, be performed harmlessly by using a wide-mouthed cylinder of not too great dimensions. A loud report is heard in this case, because the steam at the moment of its formation occupies a much larger volume at the high temperature of the combustion than the mixture of the original gases, and as a result the air is suddenly ejected with violence. When the explosion occurs in a closed vessel, no sound is heard (*cf.* e.g. Fig. 13, p. 27).

The temperature to which detonating-gas must be heated to explode is found to be about 700°. At a lower temperature combination between hydrogen and oxgyen also takes place, but not instantaneously, as in explosions; the lower the temperature, the slower the process. When, therefore, no change in cold detonating-gas is observed even in the course of several years, we must attribute the fact to the extraordinary slowness of the process at ordinary temperatures. A simple calculation will make this plain. Bodenstein observed that, when detonating-gas is heated at 509° for 50 minutes, 0.15 of the whole is changed to water. Now it is a general rule that, when the temperature sinks 10°, a chemical reaction becomes about twice as slow; at 499° it would thus take 100 minutes till the 0.15 part of the gas had formed water. At the ordinary temperature, say at 9°, it would be 50×2^{50} minutes, that is about 1.06×10^{11} years. The same can be said of all chemical reactions. When we see that wood, sulphur, etc., burn quickly at higher temperatures, we must admit that oxidation takes place also at ordinary temperatures, though so slowly that we cannot perceive it. Moissan, however, succeeded in proving that charcoal at 100° and sulphur at ordinary temperatures are oxidized very slowly in a current of oxygen.

Hydrogen is not only able to unite with free oxygen, but it also has the power to withdraw oxygen from many of its compounds. The action of hydrogen on a compound is called, in general, **reduction.** This action is often a very useful means of determining whether a compound contains oxygen, since the latter, if present, will usually unite with the hydrogen to form water. Copper oxide may serve as an example of the application of this method. A little is placed in a tube, hydrogen is led over it, and heat is then applied; one soon sees the black oxide change to red copper, and water depositing in drops on the colder parts of the tube. Many other oxides can be similarly reduced, e.g. iron oxide, lead oxide, etc.

THE CONSERVATION OF MATTER.

14. The quantitative relationships in oxidizing and reducing processes, such as have been discussed in § 13, i.e. the relations of the masses of the substances participating in the changes, may be used to elucidate a very important law. A definite amount of copper powder, for example, may be placed in a tube and the weight of the tube with the powder ascertained. Oxygen is then led over the copper at a high temperature. The apparatus should be so arranged that the volume of the oxygen which combines with the copper can be measured. When the oxidation process has proceeded for some time, the tube containing the oxidized copper is allowed to cool and then weighed. The weight is found to have increased, and the increase is just equal to the weight of the volume of oxygen used up. Thereupon hydrogen is passed through the tube with the copper oxide and heat applied. Here also arrangements should be made for measuring the volume of hydrogen consumed in reduction. The reduction is allowed to go on until all the copper oxide is transformed back to copper. When the tube and powder are subsequently weighed, they will be found to have reassumed their original weight. The water that forms can be absorbed by a substance like quicklime or concentrated sulphuric acid and weighed. It will be found equal in weight to the loss of weight of the copper oxide on changing to copper plus the weight of the consumed hydrogen.

In these cases, therefore, the combined weight of the reacting substances before and after the reaction is the same. Copper + consumed oxygen weighs just as much as copper oxide; copper oxide + consumed hydrogen weighs just as much as copper + water; and, finally, the regained copper weighs just as much as that originally taken. The substances can be changed into different states, but their weight remains unaltered. This phenomenon is observed without exception in chemical actions, and we therefore accept as a law the statement that matter is indestructible, or that no matter can be lost or gained. This principle was introduced into chemistry by LAVOISIER (1743–1794).

The old Greek philosophers were already firmly convinced of the impossibility of producing or destroying matter. In all ages this belief has been the basis of philosophic thought. To LAVOISIER is due the credit of having demonstrated the practical application of the principle of the indestructibility of matter. He assumed that gravity is an inseparable attribute of all matter—concerning which a great deal of doubt still existed—and that the combined weight of the substances concerned must therefore be the same before and after a chemical reaction.

The theory of knowledge teaches that the principle of the indestructibility of matter lies originally at the basis of our thinking. It is entirely incorrect to suppose that it was established by experimentation; on the contrary, we test the correctness of our experimental results by ascertaining in how far they conform to this principle. This can be easily understood in the above case of the oxidation and reduction of copper. In performing this experiment one finds that the weight of copper + oxygen is *not* exactly equal to that of the copper oxide formed. Even after several repetitions slight differences are still found. Because we feel that there must be absolute equality, we attribute these differences to imperfections in our instruments, and we consider our instruments improved if they enable us to approach nearer the complete equality of the weights before and after the experiment. Nevertheless, we are unable to really observe an absolute equality.

WATER.

15. Water was regarded as an element for many centuries. Not until 1781 did CAVENDISH discover that, when a mixture of hydrogen and air or oxygen explodes, water is formed. Being, however, a supporter of an erroneous theory (§ 106), he failed to realize the importance of his discovery. LAVOISIER in 1783 repeated this experiment and comprehended it as a synthesis of water, as we still do to-day.

With the aid of the apparatus pictured in Fig. 7, this synthesis can be easily demonstrated. The hydrogen is generated in the two-necked (WOULFF) bottle from zinc and sulphuric acid. In order to free the gas from water vapor, it is passed through the horizontal tube, which contains chloride of calcium or bits of pumice-stone soaked in sulphuric acid. The dry gas is ignited and, as it burns, water is gradually deposited on the walls of the bell-jar.

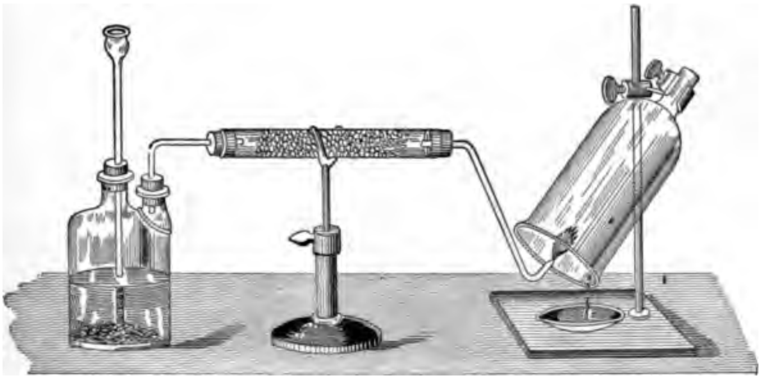

FIG. 7.—COMBUSTION OF HYDROGEN.

In addition to this direct synthesis from its elements there are other ways of obtaining water. For example, many compounds, such as the blue crystals of copper vitriol, give off water when heated.

The formation of water by the action of hydrogen on oxygen compounds was illustrated (§ 13) in the reduction of copper oxide. On the other hand, it is also produced by the action of oxygen on certain hydrogen compounds. This is seen, for example, in the burning of alcohol.

Finally, water can result from the reaction of a hydrogen compound with one of oxygen. This is the case when ammonia gas (§ 111) is led over hot copper oxide.

The synthetic methods of preparing water, such as the above-named and many others, possess, however, merely theoretical importance. Even when water is wanted in a perfectly pure state, natural water is resorted to. This contains solids and gases in solution, which must be eliminated. Its purification is accomplished by distillation. An apparatus well suited to this purpose is shown in Fig. 8. High pressure steam and electricity are often used for heating instead of the flame.

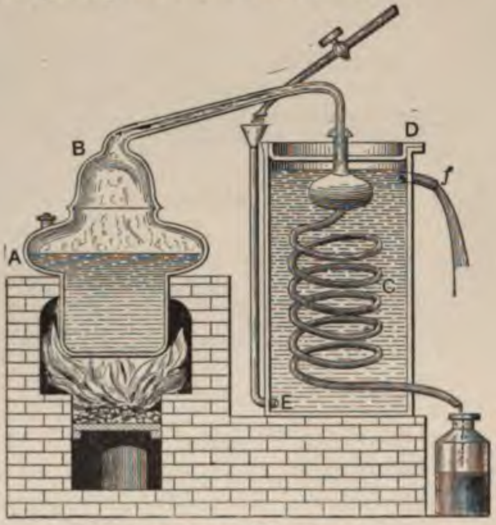

FIG. 8.—PURIFICATION OF WATER BY DISTILLATION.

Water is placed in the retort *A*, which rests over the fireplace, and boiled. The dissolved gases are first driven off; the hot steam follows, passing through the dome *B* into the condensing coil ("worm") *C*, which is cooled by water in the vessel *D*. The condensed water, now pure, flows down into the bottle; the solid substances that were dissolved in the water remain in the retort. The cooler *D* is supplied with cold water through a tube, entering near the bottom, while the heated, and therefore specifically lighter, water flows out near the top. The steam thus meets with cooling-water of a lower temperature as it passes down the worm, and is in this way very completely condensed (principle of the counter-current).

A single distillation is usually insufficient for the complete elimination of all gaseous and solid constituents. For this purpose the operation must be repeated in an apparatus of platinum (tin is less satisfactory) with a condensing coil of the same metal, and only the middle fraction collected.

An excellent criterion for the purity of water is to be found in the measurement of its electrical resistance. Very pure water conducts the electric current scarcely at all. KOHLRAUSCH found the conductivity at 18° of the purest water obtainable to be $k=0.038\times10^{-6}$ expressed in reciprocal ohms; by this is meant the conductivity of a body a column of which 1 cm. long and 1 cm. square in cross-section has a resistance of 1 ohm. The magnitude of the resistance of such water is better understood by comparing it with resistance of copper. 1 cu. mm. of this water has at 0° the same resistance as a copper wire of the same cross-section and 25 million miles long; it could be strung around the earth's equator one thousand times. The slightest traces of salts or even contact with the atmosphere cause a market increase in its conductivity.

PHYSICAL PROPERTIES.

16. Water at ordinary temperatures is an odorless, tasteless liquid, showing no color in thin layers. On looking through a layer 26 meters thick, SPRING observed a pure dark-blue color. The thermometer-scale of CELSIUS is fixed according to the physical constants of water, its freezing-point being called 0° and its boiling-point at 760 mm. pressure 100°. These two points are dependent on the pressure. An increase of pressure lowers the freezing-point (0.0075° per atmosphere). This is the reason why ice melts under high pressure. Water possesses the very uncommon property of having a maximum of density (minimum of volume) at a definite temperature. The volume of almost all other substances increases with rising temperature, but here it diminishes up to 3.945°, above which temperature water expands as heating continues. During the transformation of water to ice the volume increases considerably. One vol. water at 0° yields 1.09082 vol. ice of the same temperature.

The specific heat of water is greater than that of a vast majority of other substances. Its latent heat of fusion is 79 Cal., its latent heat of vaporization 536 Cal. Water is extensively used as a solvent. Numerous substances dissolve in it to a greater or less degree. There are many liquid substances that mix with water in all proportions, and many, also, which do not. (See § 7.)

The remarkable physical properties of water play a very important rôle in nature. As this subject is extensively discussed in physics, meteorology and geology, we can pass over it here very briefly. The marked increase of volume during the transformation of water into ice, as a result of which the specific gravity becomes less, is the reason why ice floats and the water below remains liquid. The temperature of the deepest layers of water very seldom gets lower than 4° C., for, when a layer reaches this temperature, it is at the point of greatest density and therefore sinks to greater depths, where it is protected from farther cooling by the poor conductivity of the upper layers. These two phenomena together prevent the entire freezing of the rivers and seas in winter to a solid mass of ice, which would necessarily take place if ice were denser than water and the maximum density point of water were not above 0°. The fact that water freezes merely at the surface not only makes the existence of water animals possible, but is also of very great influence on the climate. If every body of water froze solid in winter, the heat of summer would be insufficient to melt all this ice, the latent heat of fusion and the heat capacity of water being so great. In our present temperate zone there would be a climate like that of the polar regions, and a large part of Europe would therefore be uninhabitable.

The expansion of water on freezing is moreover a very important factor in the disintegration of rocks. During rains, etc., the water percolates into the cracks of the rocks and, if it freezes, the force with which it expands is so great that the cracks are gradually widened, until the rock at last falls to pieces.

Then, too, as a solvent, water affects the minerals in various ways. In this respect also it is a very substantial geological factor.

NATURAL WATER.

17. Water, as it occurs in nature, is by no means chemically pure. It may contain solid matter in suspension as well as substances, either solid or gaseous, in solution. The purest natural water is *rain-water*. This has really passed through a natural process of distillation, the water on the earth's surface being vaporized by the sun's heat and condensed again by contact with colder portions of air, whereupon it falls in the form of rain. Nevertheless it contains dust particles (in large cities more, of course, than in the country) and gases from the air, as well as traces of ammonium salts.

Spring- and *well-waters* contain in 10,000 parts about 1–20 parts of solid matter, consisting largely of lime salts. Well-water that contains much lime is called *hard* (§ 259). Well-water also contains some carbonic acid and air in solution, both of which give it its refreshing taste; distilled water tastes flat.

Natural water is used extensively for drinking purposes. When it comes out of a soil that is contaminated by decaying organic matter, as is the case in many large cities, it is injurious to health, principally on account of the presence of bacteria. It can be freed from these by filtration through a PASTEUR-CHAMBERLAND porcelain filter (Fig. 9).

This consists essentially of a hollow cylinder of porous porcelain (called a "candle") *A*, through whose walls the water is forced by its own pressure. The lower end of the candle opens into the nozzle.

In large cities it has been found much more practicable to purify the well- or river-water at the central station and to pipe it thence to the various houses. Epidemic diseases have really decreased remarkably since the introduction of the methods of modern sanitary science.

A water which contains so many substances in solution that it has a definite taste or a therapeutic effect is called a *mineral water*. There are very many kinds of mineral waters, differing according to the amount and kind of dissolved matter they contain. We distinguish between saline waters containing common salt, bitter waters with magnesium salts, sulphurous waters with sulphuretted hydrogen, carbonated waters with carbonic acid, chalybeate waters with iron, and many others. Detailed analyses of the mineral waters of numerous watering-places are accessible in works on balneology.

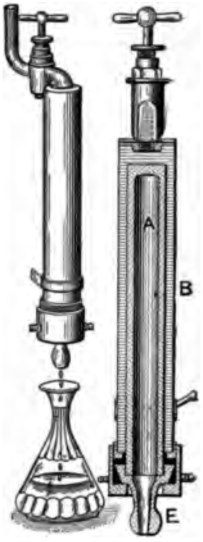

FIG. 9.—PASTEUR-CHAMBERLAND FILTER.

Sea-water contains about 3% of salts, of which 2.7% is common salt. A large number of elements, viz., about thirty, have been found in sea-water, although the most of them exist there only in extremely small quantities.

It was stated above (§ 16) that pure water is blue. The color of the rivers, lakes and seas varies, however, through many nuances from pure blue to brown. This variation is due principally to the presence of more or less brownish-yellow humous (marshy) substances or an extremely fine floating slime. Both conditions can produce a brownish-yellow color. It is easily seen how the combination of blue and yellow or brown may bring about the various blue, green or brown tints in natural waters.

COMPOSITION OF WATER.

18. Decomposition.—It was stated above that water can be obtained by direct combination of hydrogen and oxygen; inversely, it can be decomposed into these same elements.

In the flask *A* (Fig. 10) some water is heated till it boils vigorously. A strong electric current is then sent through the wire *a c b*, so that the fine platinum wire *c* glows intensely. This heat partially decomposes the water vapor into hydrogen and oxygen, which pass out through the tube *d* and are collected in the cylinder *C*. This gas mixture is nothing but the explosive mixture (§ 13) of hydrogen and oxygen, as can be easily proved by applying a flame.

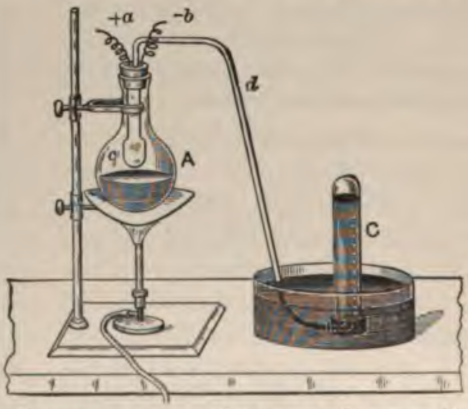

FIG. 10.—DECOMPOSITION OF WATER BY GLOWING PLATINUM.

Many metals decompose water on contact, the hydrogen being set free and the metal uniting with the oxygen. Potassium and sodium effect this decomposition at ordinary temperatures (§ 11); iron, zinc and other metals require a higher temperature, iron, e.g., acting at red heat.

19. Let us now study the quantitative composition of water, i.e. determine the relative amounts of hydrogen and oxygen present. For this purpose both the analytic and synthetic methods can be used.

(*a*) *The Analytic Method.*—When an electric current is passed through water to which has been added a little sulphuric acid, the water is decomposed. If the gases evolved at the electrodes are collected separately, it is found that for every 1 vol. oxygen 2 vols. hydrogen are given off. A suitable apparatus for this experiment is shown in Fig. 11.

Since 1 liter of hydrogen weighs 0.0899 g. and 1 liter of oxygen weighs 1.4296 g., both at 0° and 760 mm. pressure, the weights of 2 vols. hydrogen and 1 vol. oxygen must bear to each other the ratio of $2 \times 0.0899 : 1.4296$, or $1 : 7.943$.

(*b*) *The Synthetic Method.*—As early as 1820 the reduction of copper oxide by hydrogen was employed for this purpose by BERZELIUS; in 1834, also, by DUMAS and STAS. A weighed amount of carefully dried copper oxide is heated in a current of hydrogen and water is formed, which is collected and weighed. The weight of the oxygen given up by the copper oxide is found from the difference between the weight of the copper oxide used and that of the resulting copper. The weight of the hydrogen contained in the water collected is therefore equal to the difference in weight of water and oxygen.

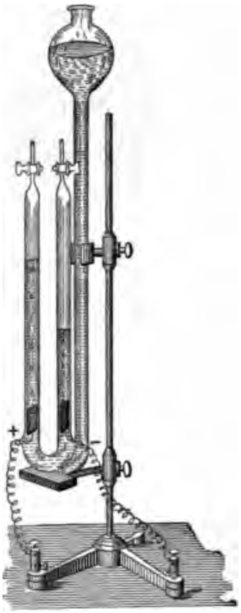

FIG. 11.—ELECTROLYSIS OF WATER.

The apparatus used for this experiment is represented in Fig. 12. In *A* the hydrogen is generated from zinc and dilute sulphuric acid. It is then passed through the permanganate solution in the wash-bottle *B* to free it from impurities, and also through the U-tubes *C*, *D* and *E*, containing calcium chloride, sulphuric acid and phosphorus pentoxide, respectively, for drying it. In *F* is placed the copper oxide, which is carefully weighed together with the tube. The water that forms is condensed in *G*, the U-tube *H* being attached to absorb any escaping water vapor. At the completion of the experiment, *F*, with its contents, is again weighed, likewise *G* and *H*; the differences in weight indicate the amount of water formed. Dumas and Stas found in this way that 100 parts (by weight) of water consist of 11.136 parts of hydrogen and 88.864 parts of oxygen, or, in other words, that the mass-ratio of these elements is 1:7.980, a relation which agrees with that obtained in (*a*) within the range of the unavoidable experimental error.

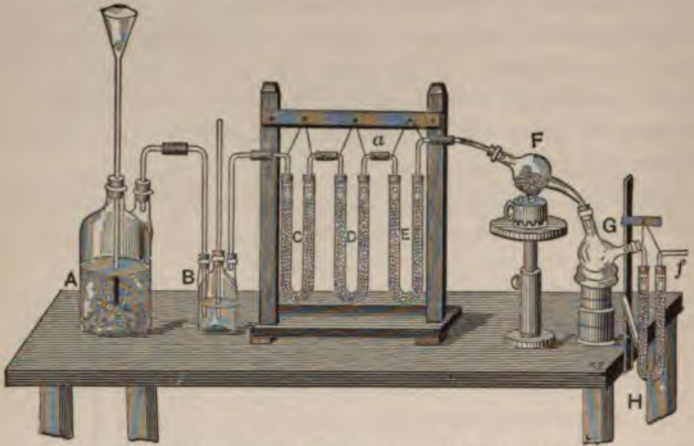

Fig. 12.—Synthesis of Water after Dumas and Stas.

Another synthetic method, which is especially adapted to the lecture-table, consists in mixing hydrogen and oxygen and determining in what volume-ratio these gases unite. For this purpose an apparatus (Fig. 13) described by Hofmann is best employed.

Hydrogen and oxygen in different proportions by volume are introduced into the arm of the U-tube, which can be closed by a stop-cock at the top: the cock is thereupon closed and the open arm tightly stoppered with a cork. The mixture is then exploded by an induction spark, the volume of air enclosed on the other side acting as a cushion to moderate the severe shock on the mercury, which might otherwise break the apparatus. It is found that *only* when the volumes of hydrogen and oxygen bear to each other the ratio 2:1 does the *entire* gas mixture disappear, a slight coating of tiny drops of water appearing in its place on the inside of the glass. In case more hydrogen or more oxygen than the ratio calls for is let into the tube, the excess is found to remain after the explosion.

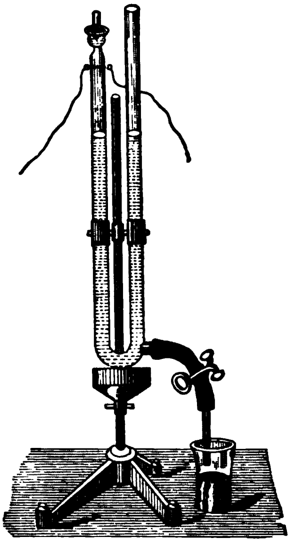
FIG. 13.—HOFMANN'S APPARATUS FOR THE SYNTHESIS OF WATER.

From these experiments, analytic and synthetic, it follows that *water has a constant composition;* it consists of 2 vols. of hydrogen and 1 vol. of oxygen, or of 1 part, by weight, of hydrogen to 7.943 parts of oxygen.

COMPOUNDS AND MIXTURES.

20. In water we have become acquainted with a substance which is different in many and important respects from the elements of which it is composed. We have further seen that the elements in it bear to each other a fixed relation by weight. Such substances are known in very large number. Copper oxide, mercury oxide, sulphuric acid, potassium chlorate, common salt, soda and many others already mentioned belong to this class. In each of these, no matter how obtained, we discover by analysis or synthesis a definite proportion between the elements composing it. Such substances are called **compounds.**

In addition to the characteristics mentioned—difference of properties from those of the elements and constant composition—we find that the compounds also have constant physical properties.

Under the same pressure water always has the same melting-point and the same boiling-point, in whatsoever way it may have been obtained; salt always crystallizes in the same crystal system; soda, at a definite temperature, always requires the same amount of water for solution, etc.

When elements or compounds are brought together without any chemical action on each other taking place, we have a **mixture** of these elements or compounds. The number of possible mixtures is, of course, unlimited. They are distinguished from compounds by the following characteristics:

In a mixture the properties of the components reappear in many and important respects. Gunpowder, for example, is a mixture of sulphur, charcoal and saltpetre. The latter is soluble in water; sulphur dissolves in carbon disulphide; charcoal is insoluble in both. These properties are still evident in the constituents of gunpowder. In a mixture of sulphur and iron filings one can detect with a microscope the yellow grains of sulphur and the black particles of iron. The iron can be drawn out with a magnet; the sulphur dissolved out by carbon disulphide. If, however, a mixture of 7 parts iron and 4 parts sulphur is heated, a glow passes through the powder and a compound of both—iron sulphide—is formed, whose properties are entirely different from those of its elements. It is non-magnetic and insoluble in carbon disulphide and under the microscope only a homogeneous scoriaceous mass is seen. The constituents of a mixture, since they still preserve their properties, can often be separated from each other by *mechanical means*, e.g. by the use of microscope and tweezers, by sifting, by treatment with solvents, by washing, etc.

In a mixture the ratio of the constituents can vary in all proportions. There are, for example, many sorts of gunpowder, distinguished from each other by the proportions in which their constituents are mixed. When 1 part sulphur and 100 parts iron, or, on the other hand, 1 part iron and 100 parts sulphur, are mixed, we have in either case a mixture of both elements, possessing hardly the same, but at least analogous, properties.

Moreover, a mixture often has no constant physical properties. Water has a constant boiling-point; the boiling-point of a mixture of benzene and turpentine, however, rises gradually as the more volatile component, benzene, distils off. The melting-point of sulphur is constant and can be accurately determined; that of a mixture of tin and lead differs according to the proportion of the elements and is in many proportions not at all sharp, there being only a softening instead of real fusion.

In the examples cited here the distinction between a compound and a mixture is well marked. There are, however, other instances where this is not the case and where it is therefore very difficult to know whether one is dealing with a compound or a mixture. We shall meet with many examples of this later. There is, however, *one* way whereby a compound can be distinguished from a mixture, viz., by ascertaining whether or not the substance, prepared in different ways, has a constant composition.

PHENOMENA ACCOMPANYING THE FORMATION OR DECOMPOSITION OF A COMPOUND.

The most common phenomenon of this sort is an elevation or depression of temperature, i.e. an evolution or absorption of heat (caloric effect). Sometimes the rise of temperature is so great that light is produced. A decomposition or a combination can be so violent that it causes an explosion. In other instances electricity may be produced by chemical action. All these facts may be comprised in this statement: *Chemical action results in a change in the energy-supply of the reacting substances.*

EXPLANATION OF THE CONSTANT COMPOSITION OF COMPOUNDS.—ATOMIC THEORY.

21. It was stated that constant composition is the distinctive characteristic of a chemical compound. The proportions in which elements unite to form a certain compound are always the same. This **Law of Constant Composition** (definite proportions) was finally established by PROUST in the beginning of the nineteenth century, and at about the same time DALTON offered an explanation of it which is still accepted and may be considered as the foundation of theoretical chemistry.

This explanation involves a hypothesis as to the constitution of matter. It is possible to regard matter as infinitely divisible; according to human conception the smallest particle that can really be obtained is still capable of division into an infinite number of others. However, even the ancients were of the opinion that there must be somewhere a limit to the divisibility and that we must finally arrive at particles incapable of further division, the **atoms.**

In the fifth century B.C. there existed a school of philosophy, that of the *Eleatics* (so called from the city of ELEA), whose most prominent representative was PARMENIDES. He taught that everything that exists cannot be otherwise conceived than as unchangeable; transformation of the existent, which was thought to have never originated and to be at the same time unalterable, was held by them to be inconceivable. These theses they regarded in a certain sense as axioms, i.e. statements of truths which are accepted without proof. Daily experience teaches one nevertheless that transformation does occur in that which exists, a fact that led them to suppose that everything observed by men is merely appearance.

Three theories were proposed in the same century which aim to form a bridge between the doctrine of the unalterable existent and the experience that points toward continuous change. These theories originated with EMPEDOCLES, ANAXAGORAS, and the *Atomists*, LEUCIPPUS and DEMOCRITES. The immutability of the existent is disposed of by ascribing it to extremely small unchangeable and indestructible particles; every change is thought to depend on the movement of these smallest integral particles toward or away from each other. EMPEDOCLES and ANAXAGORAS assume in this connection an infinite divisibility; the Atomists, on the contrary, regard the world as built up of indivisible particles, atoms, all of which consist of the same primordial substance but differ in form and size.

Now DALTON has used this conception of the ancients regarding the atom to explain the fact that the combining weights are constant. The atoms of the various elements, he assumes, have different weights; the atoms of the *same* element are alike in weight. A compound of two elements is therefore produced by the association of atoms of these elements. Such a combination of two or more atoms is called a **molecule.** It is obvious that these suppositions lead directly to the *law of constant proportions;* for, if copper oxide is formed by an atom of copper uniting with an atom of oxygen to make a molecule of copper oxide, its composition must, according to the above hypothesis, be constant.

DALTON deduced another conclusion from his hypothesis, and confirmed the same experimentally. He observed that oxygen unites not only with *one* very definite amount of nitrogen oxide, but also with twice as much, not, however, with any intermediate amount. He also showed by the investigation of marsh-gas and olefiant gas, both of which are made up of only carbon and hydrogen, that the former contains twice as much hydrogen to a certain weight of carbon as the latter. It is readily seen how such observations can be explained on the basis of the atomic theory; in one case 1 atom of carbon is in combination with n atoms of hydrogen; in the other with $2n$ atoms. The observations of DALTON were subsequently confirmed and extended, especially by BERZELIUS. The following statement is therefore now accepted as a law: *When two elements combine to form more than one compound, the different weights of the one element which unite with one and the same weight of the other element bear a simple ratio to each other.* This is the **Law of Multiple Proportions.**

22. The absolute weight of the atoms is not exactly known. It is so small that no one has as yet succeeded in determining either the size or the weight of the atoms (or of the molecules) except approximately.

The following data may give an idea of their probable magnitude:

1. Many substances, e.g. musk and certain organic sulphur compounds, possess an extremely powerful odor. If a bottle containing such a substance is opened in a room for a few moments, the odor can soon be detected throughout the entire room; nevertheless, even a sensitive balance fails to show any perceptible decrease in the weight of the bottle. The extremely small amount of the substance which evaporates contains, therefore, such a large number of molecules that when these are distributed in a relatively large space, the odor can be detected in all parts. BERTHELOT proved that a particle of musk weighing 10^{-11} gr. can still be perceived by its smell. A molecule of it cannot have a greater weight than this.

2. Certain dyestuffs like fuchsine are extremely intense. A solution containing only 7×10^{-6} gr. per cc. shows the color with certainty in a single drop (35 drops per cc.). The eye can therefore detect 2×10^{-7} gr. fuchsine. A molecule of the latter must be fully as small as that. By means of fluorescent substances this limit can be still further extended. SPRING found that a solution of fluorescein clearly showed the characteristic yellow-green fluorescence at a dilution of 10^{-15} gr. per cc. when a beam of electric light rays was focussed upon the solution. As the quantity of liquid in the focus was about 1 cu. mm., the fluorescence must have been caused by 10^{-18} gr., which is, therefore, the upper limit for the weight of one molecule of fluorescein.

3. It is assumed that the molecules of a gas are free to move in all directions. As a result, the molecules must encounter each other very frequently. Moreover the length of the free path through which the gas molecules may move without collision depends on their size. This free path can be calculated, as is shown in physics, from measurements of the diffusion, heat-conductivity and internal friction of the gases. When it is known, we can estimate the size of the molecules. Thus VAN DER WAALS was able to arrive at the following approximations: The number of molecules in 1 $mm.^3$ air at 0° and 760 mm. Hg pressure is represented by a number of seventeen figures; 1 $mm.^3$ air weighs, however, only 1.3×10^{-6} g. The weight of one atom of hydrogen in milligrams was calculated to be a number of the 10^{-21} order.

CHEMICAL SYMBOLS.

23. The absolute weight of the atoms is thus only approximately known. Nevertheless, their **relative weights, i.e.** the weights of the atoms of the various elements, when that of a *certain* element is *arbitrarily fixed,* have been determined in a variety of ways. These relative weights, which are known as **atomic weights,** are expressed by symbols, that were introduced by BERZELIUS and are of great convenience in the representation of compounds and the formulation of chemical processes. Such a symbol stands not only for the element concerned, but also for the relative weight of an atom of that element. If the atomic weight of copper is 63.3 and that of oxygen 16, the symbol Cu indicates 63.3 parts by weight of copper, the symbol O 16 parts by weight of oxygen. It has been determined that in copper oxide one atom of copper is combined with one atom of oxygen; copper oxide is therefore represented by the formula CuO, which expresses, first, that we are dealing with a compound of copper and oxygen, and, second, that 1 atom (63.3 parts by weight) of copper is united in it to 1 atom (16 parts by weight) of oxygen. Many compounds contain several atoms of the same element. This is indicated by placing the proper figure to the right of and below the symbol. Sulphuric acid, for example, contains 2 atoms of hydrogen (H), 1 atom of sulphur (S) and 4 atoms of oxygen (O) in the molecule. Its formula is, therefore, H_2SO_4.

Chemical actions can be very simply represented by the use of these formulæ; thus, the decomposition of mercuric oxide into oxygen and mercury by

$$HgO = Hg + O;$$

that of potassium chlorate into oxygen and potassium chloride by

$$\underset{\text{Potass. chlorate.}}{KClO_3} = \underset{\text{Potass. chloride.}}{KCl} + 3O;$$

the generation of hydrogen from zinc and sulphuric acid by

$$Zn + H_2SO_4 = 2H + ZnSO_4.$$

In such **equations** the same atoms and the same number of each must appear on both sides, in accordance with the principle of the Indestructibility of Matter.

Besides the atomic weights, we quite frequently use equivalent weights. These are the weights of the elements which combine with a unit amount of a certain standard element. One part of hydrogen combines, for instance, with 35.5 parts of chlorine and with 8 parts of oxygen. These amounts of hydrogen, chlorine and oxygen are equivalent to each other. The atomic weight is either equal to the equivalent weight or a multiple of it.

STOICHIOMETRICAL CALCULATIONS.

24. If the formulæ of the compounds are known—the means of ascertaining these will be discussed in detail later—and the atomic weights of the elements composing them also known, it is very easy to calculate the weights that enter into reaction in all chemical changes. A couple of examples may serve to make this clear.

1. It is required to know *how many liters of oxygen at 0° and 760 mm. pressure can be obtained by heating 1 kilogram of mercuric oxide.*

The atomic weight of mercury is 200, that of oxygen is 16; mercuric oxide, HgO, is, therefore, 200+16. Out of these 216 parts by weight of mercuric oxide 16 parts of oxygen can be obtained by heating, i.e. from 1 kilo (=1000 g.) can be obtained $\frac{1000 \times 16}{216} = 74.07$ g. Since 1 l. oxygen at 0° and 760 mm. pressure weighs 1.4296 g., 74.07 g. occupy a volume of $\frac{74.07}{1.4296} = 51.8$ l.

2. *How much water can be formed from the hydrogen obtained*

by the interaction of 1 kg. zinc and the corresponding amount of sulphuric acid?

The reaction of zinc and sulphuric acid is expressed by the equation

$$Zn+H_2SO_4=ZnSO_4+2H$$

and the combustion of hydrogen to form water by the equation

$$2H+O=H_2O.$$

From these equations it follows that the hydrogen formed by the action of 1 atom of zinc yields 1 molecule of water. For every atom of zinc we obtain, therefore, 1 molecule of water. The atomic weight of zinc is 65, the molecular weight of water 18; therefore 65 parts of zinc correspond to 18 parts of water. 1 kg. zinc must yield $\frac{1000\times 18}{65}=276.9$ g.

3. *How many grams of potassium chlorate are necessary to produce enough oxygen to oxidize 500 g. copper to copper oxide?*

The reactions concerned are

$$KClO_3=KCl+3O \quad \text{and} \quad Cu+O=CuO.$$

Hence 3 atoms of copper can be oxidized with the oxygen derived from 1 molecule of potassium chlorate. For every 3 atoms of copper 1 molecule of potassium chlorate must be consumed. The molecular weight of the latter substance is $39+35.5+3\times 16=122.5$; the atomic weight of copper is 63; for every 63 parts of copper $\frac{122.5}{3}=40.8$ g. potassium chlorate are therefore required. Hence 500 g. copper require $\frac{500\times 40.8}{63}=323.8$ g. potassium chlorate.

In most chemical computations *gram-molecules* are employed, these being the molecular weights of the substances in grams. The abbreviation *mole* has been suggested by Ostwald for this term. Thus "1 mole" copper oxide means $63+16=79$ grams of it.

The molecular weight in milligrams is called a *millimole*. In the same way we may speak of a *kilomole*, etc.

It is now customary to take the atomic weight of oxygen as 16. The atomic weights of the remaining elements then have the values that are given in the table on the inside of the back cover of this volume.

A few years ago there was established a permanent international commission whose duty it should be to revise the table of atomic weights critically every year. Those values are accepted as the "international atomic weights" which appear to be the most probable among the determinations that have been published.

The symbols whose derivation is not at once apparent are taken from the Latin names of the elements; e.g., Sb from *stibium*, Au from *aurum*, Cu from *cuprum*, Hg from *hydrargyrum*, Pb from *plumbum*, Sn from *stannum*, Fe from *ferrum*, and Ag from *argentum*.

The atomic weights in the table are carried out to as many decimal places as may be accepted with certainty. For many purposes it is sufficient to use round numbers, such as N = 14, Br = 80, etc.

The acceptance of 16 as the atomic weight of oxygen has a historic reason. For a long time hydrogen was taken to be 1; it was believed that the ratio of the atomic weights of hydrogen and oxygen was 1 : 16. Inasmuch as the atomic weights of most elements are determined from the composition of their oxygen compounds, the basis is really O = 16 and not H = 1. This made no difference, so long as the proportion H:O = 1:16 was considered accurate. Even when the ratio was later found to be a different one (according to investigations of MORLEY and of W. A. NOYES the ratio 1: 15.88 may now be regarded as very accurately determined), it was still the simplest plan to preserve O = 16 as the basis, since a change would necessitate a complete recalculation of all the atomic weights, and this necessity would moreover recur as often as a new refinement of methods of investigation brought about a change in the ratio H:O.

CHLORINE.

25. Chlorine does not occur free in nature, since it acts upon the most diverse substances at ordinary temperatures. In compounds, however, it occurs extensively. Common table-salt is a compound of sodium and chlorine. Various other metallic chlorides are also met with in nature.

Chlorine gas can be obtained by the *direct* decomposition of certain chlorine compounds; thus:

1. By the electrolysis of hydrochloric, or muriatic, acid (i.e. a solution of hydrogen chloride, HCl, in water). Chlorine is given off at the positive pole (anode), hydrogen at the negative (cathode).

The *indirect* decomposition of its compounds offers, as in the case of hydrogen (§ 11), the *most practicable* methods of obtaining the element. They are all based on the oxidation of the hydrogen of hydrochloric acid, whereby water is formed and chlorine liberated.

2. Commercially, as well as in the laboratory, manganese dioxide, MnO_2, is frequently used as the oxidizing agent:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl.$$

It is very often convenient to generate the hydrochloric acid from salt and sulphuric acid in the same vessel with the manganese dioxide. The two reactions thus proceed simultaneously:

$$\text{I. } NaCl + H_2SO_4 = NaHSO_4 + HCl.$$
$$\text{II. } 4HCl + MnO_2 = MnCl_2 + 2H_2O + 2Cl.$$

3. Other commonly used oxidizing agents are chloride of lime and potassium dichromate; e.g.

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 6Cl.$$

4. The oxygen of the air can also serve as the oxidizing agent when a catalyzer is present. For this purpose a mixture of air and hydrogen chloride is passed over porous bricks at 370–400°, which are soaked with copper sulphate solution:

$$2HCl + O = H_2O + Cl_2.$$

This method, which is known as the *Deacon process*, is used commercially. The copper sulphate is here the catalyzer.

The progress of chemical changes is often modified by the mere presence of a substance which has the same chemical composition after the reaction as at the beginning. Such a substance is termed a *catalyzer* and the action which it exerts is called *catalysis*, or *catalytic action*. The quantity of the catalyzer necessary to exert a perceptible influence is often very small. This is the case, for example, in the combination of hydrogen and oxygen in the presence of platinum as a catalyzer (§ 13, p. 16).

A minute trace of platinum sponge brought into contact with detonating-gas accelerates the formation to such a rate that the reaction takes place very quickly and can even become explosive. In the DEACON process, also, a small quantity of copper sulphate suffices to bring into reaction unlimited quantities of hydrogen chloride and oxygen.

At the temperature of 370–400° there is practically no reaction between oxygen and hydrogen chloride without the catalyzer. That there must nevertheless be a reaction, although a very slow one, can be demonstrated by the same reasoning as in § 13. The catalyzer therefore does not cause a reaction, but only accelerates it. OSTWALD compares its action to that of oil on the axles of a machine which move with very great friction. When oiled, the machine will go much faster, notwithstanding that the force of the spring (here the energy of the chemical reaction) has not changed A further point in the analogy is that the oil is not consumed.

In most cases of catalysis it can be proved that the catalyzer takes part in the reaction but at the end of it reappears in its original condition. In the platinum catalysis of detonating-gas, for example, the metal unites with the oxygen, whereupon the resulting compound reacts with the hydrogen, giving water and metallic platinum. The phenomenon of catalysis is universal. OSTWALD thinks it probable that there is no kind of chemical reaction that cannot be influenced catalytically and that there is no substance, element, or compound, which cannot act as a catalyzer.

Catalyzers may accelerate or retard reactions; at present, however, much more is known of the first than of the second kind.

26. *Physical Properties.*—Chlorine is yellowish-green (hence its name, which is derived from χλωρός, greenish-yellow) and has a disagreeable odor. Its specific gravity is 2.45, taking air as unity, or 35.45, based on O = 16. 1 l. chlorine weighs, therefore, 3.208 g. at 0° and 760 mm. pressure. At −34° it becomes liquid under ordinary pressure; at −102° it solidifies and crystallizes. Its critical temperature is 146°. Liquid and solid chlorine are yellow. Chlorine gas dissolves in about one-half its volume of water. The aqueous solution bears the name "chlorine-water." It can, therefore, not be collected over water, but a saturated salt-solution may be used, in which it is only slightly soluble. The most convenient way to fill a vessel with it is by displacement of air, the gas being conducted to the bottom, where it remains and drives out the air above, because the chlorine is denser.

27. *Chemical Properties.*—Even at ordinary temperatures, chlorine combines with many elements and acts on many compounds. If perfectly pure chlorine is mixed with an equal volume of hydrogen, the two unite in direct sunlight, causing an explosion. If the chlorine is impure or the sunlight diffused, combination occurs slowly. When a hydrogen flame is introduced into chlorine gas, it continues to burn, with the formation of hydrogen chloride. Many metals combine with chlorine with the evolution of light, e.g. copper (in the form of imitation gold-leaf), finely powdered antimony, molten sodium, etc. The precious metals are in general quite resistive to chemical action. They are, however, attacked by chlorine and changed to chlorides, i.e. chlorine compounds. Gold, for instance, dissolves in chlorine-water, forming gold chloride.

Chlorine also unites readily with many non-metals, e.g. phosphorus, which burns in it with a pale flame to phosphorus chloride.

The tendency of chlorine to unite with hydrogen—its so-called *chemical attraction*, or *affinity*, for the latter—is so strong that chlorine abstracts the hydrogen from many hydrogen compounds in order to combine with it. A strip of paper dipped in turpentine burns with a sooty flame when introduced into an atmosphere of chlorine; the chlorine unites with the hydrogen of the turpentine and sets the carbon free. A burning candle continues to burn in chlorine, depositing soot (carbon) and forming hydrogen chloride. If sulphuretted hydrogen gas, H_2S, is passed into chlorine-water, hydrochloric acid and sulphur are formed.

Water is also decomposed by chlorine, oxygen being liberated:

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$

This reaction takes place under the influence of sunlight, but proceeds very slowly. It can be conveniently demonstrated as in Fig. 14. A retort is filled with dilute chlorine-water, inverted and exposed to the sunlight. After a few days a bubble of gas collects at the top of the retort, and on investigation with a glowing splinter, it is found to be oxygen.

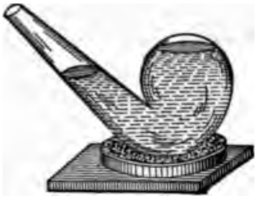

FIG. 14.—SLOW DECOMPOSITION OF WATER BY CHLORINE.

Upon this decomposition of water depends the *bleaching and disinfecting action* of chlorine and those substances which generate chlorine. In bleaching, the coloring matters—usually of an organic nature—are oxidized by oxygen to colorless substances. Bacteria are killed by oxidation. Ordinary atmospheric oxygen does not produce these effects. Litmus, for instance, which is rapidly decolorized in moist chlorine gas, is totally unaffected by the air. The particularly energetic action of the oxygen that is produced from water by chlorine is explained by assuming that it exists in an atomic condition, the **status nascens**, regarding which more will be said later (§ 38). Perfectly dry chlorine has no bleaching power.

If water is saturated with chlorine at 0°, crystals are deposited, of the composition Cl_2+8H_2O, **chlorine hydrate**. At a higher temperature these are wholly decomposed into chlorine and water.

HYDROGEN CHLORIDE, HCL, and HYDROCHLORIC ACID.

28. Hydrochloric acid, of the formula HCl (§ 31), is a gas, occurring in nature in the free state, e.g. in the gases of some volcanoes. It forms an important, although small, part of the gastric juice of man and other animals.

Some of its *methods of formation* have been already given (§ 28), viz., by direct synthesis from its elements, and also by the action of chlorine on hydrogen compounds. Moreover, it can also result from the action of hydrogen on some chlorine compounds, e.g. silver chloride, AgCl, and lead chloride, $PbCl_2$, when heated in a current of hydrogen, yield metal and hydrochloric acid:

$$AgCl + H = Ag + HCl.$$

The ordinary method of preparation is by the action of a chlorine compound on a hydrogen compound, viz., that of salt (sodium chloride) on concentrated sulphuric acid:

$$\underset{\text{Sodium chloride.}}{NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = NaHSO_4 + HCl.$$

This method is employed technically as well as in the laboratory.

The above reaction takes place at ordinary temperatures. If the sulphuric acid is to be completely used up, i.e. if all the hydrogen of the sulphuric acid is to go off with the chlorine of the salt as hydrochloric acid, the temperature of the reaction must be raised (*cf.* also § 226):

$$2NaCl + H_4SO_4 = Na_2SO_4 + 2HCl.$$

29. *Physical Properties.*—Hydrogen chloride is a colorless gas with a pungent odor. Its critical temperature is +52.3°; the critical pressure 86 atmospheres. Liquid hydrogen chloride boils at −83.7°; the solid melts at −111.1°. Specific gravity of the gas = 1.2696 (air = 1); 1 l. HCl at 0° and 760 mm. pressure weighs 1.6533 gr.

For obtaining hydrogen chloride in a pure state MOISSAN has elaborated a method which is generally applicable to gases, since low temperatures are easily attainable by means of liquid air. The freshly generated gases contain in most cases moisture and other impurities. The gases are first dried by being passed through one or two wash-bottles placed in a bath of a lower temperature than −50°. At that temperature the tension of water vapor is practically zero. The gases dried in this way are now condensed by strong cooling to the solid state. Air can then be pumped out of the vessel If the temperature is now allowed to rise, the solid mass melts first; the resulting liquid, when vaporized, gives the perfectly pure gas.

The gas fumes strongly in the air, forming a cloud with the moisture of the air. It is very soluble in water, 1 vol. water at 0° being able to absorb 503 vols. HCl gas. The aqueous solution of the gas is called "hydrochloric acid," * also *muriatic*

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* The gas itself is often called "hydrochloric acid gas."

acid. It is manufactured commercially on a large scale (§ 226). Hydrochloric acid is employed almost exclusively in the form of this aqueous solution. A solution saturated at 15° contains 42.9% HCl and has a specific gravity 1.212; it fumes vigorously in the air. The ordinary pure "concentrated" or "fuming" muriatic acid of commerce usually has a specific gravity of 1.19 and contains about 38% HCl.

Hydrogen chloride does not obey the law of HENRY (§ 9) in its behavior towards water, for its solubility in this liquid is not at all proportional to the pressure. The larger part of it is absorbed in water without reference to the pressure, and an increase of pressure causes only a small increase in the solubility. Such conduct indicates that a change in the compound has occurred; just what this change consists in we shall soon have occasion to consider (§§ 65, 66). When hydrogen chloride is led into water till the solution becomes saturated, most of it undergoes this change; only a relatively small part exists in solution as unchanged hydrogen chloride, and it is this part only that is subject to HENRY'S law. This explains why, after saturation at ordinary pressure, the amount dissolved increases much more slowly than the pressure.

30. The *chemical properties* of hydrogen chloride are found to be quite different when it is in a perfectly dry condition, e.g. condensed to a liquid, than when it is dissolved in water. In the former case it does not act on metals nor change the color of blue litmus. In the latter case just the contrary is true. Zinc, iron, and other metals, when dipped in the aqueous solution of hydrogen chloride, are vigorously attacked, hydrogen being given off. Blue litmus is turned red by the solution. Moreover, even dilute solutions taste sour. Now, there are a lot of substances that undergo a similar change of properties when they are brought in contact with water, and whose aqueous solutions possess about the same properties as those that are described here for hydrochloric acid. The nature of this change will be discussed later on (§ 65). It should be stated here, however, that these substances have a common name. They are called **acids**. *Acids have one or more hydrogen atoms that can be replaced by metals. The compounds of metals that are formed by such substitution are called* **salts**. Salts can result not only from the direct action of metals on acids, but also from the interaction of acids and **bases**. The term "bases"

includes compounds of the general type MOH, where M represents a metal. Most of them have an alkaline taste and turn red litmus blue. When sodium is dropped into water, hydrogen is generated, and a base, sodium hydroxide, is formed:

$$Na + H_2O = NaOH + H.$$

If this hydroxide is now treated with hydrochloric acid, sodium chloride and water are produced:

$$NaOH + HCl = NaCl + H_2O.$$

If we indicate an acid by the general formula AH and a base by MOH, the formation of salts from the interaction of the two may be represented thus:

$$MOH + HA = MA + H_2O.$$

A third way of forming salts is by the action of an acid upon a metallic oxide, e.g.

$$\underset{\text{Zinc oxide.}}{ZnO} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2O.$$

In general, the bases are built up from metals, the acids from metalloids.

When hydrochloric acid is added to a solution of a silver salt, for instance to silver nitrate, a decomposition of this salt takes place according to the equation

$$\underset{\text{Silver nitrate.}}{AgNO_3} + HCl = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Silver chloride.}}{AgCl}.$$

The silver chloride is insoluble, and is precipitated as a white, curdy mass. In this reaction the hydrochloric acid has liberated the nitric acid from its salt. It is also possible to liberate a base from a salt by the addition of another base:

$$AgNO_3 + NaOH = \underset{\text{Silver hydroxide.}}{AgOH} + \underset{\text{Sodium nitrate.}}{NaNO_3}.$$

Such reactions are called *single*, or *simple*, *decompositions*.

Now it can also happen that two salts exchange their metals when brought together:

$$\underset{\text{Sodium chloride.}}{NaCl}+AgNO_3=AgCl+NaNO_3,$$

so that two other salts are obtained. Such a reaction between salts is called a *double decomposition.*

We shall later have occasion to study the laws governing both of these decompositions.

COMPOSITION OF HYDROCHLORIC ACID. LAWS OF GAY-LUSSAC AND AVOGADRO.

31. The composition of hydrochloric acid is determined by the following experiments:

(*a*) When strong hydrochloric acid (a more than 23% solution) is subjected to electrolysis in a suitable apparatus (see below) it is observed that *equal volumes* of hydrogen and chlorine are evolved.

(*b*) Equal volumes of chlorine and hydrogen unite to form hydrochloric acid without leaving a remainder of either element. 2 vols. HCl are formed. Since the weight of 1 vol. Cl is 35.45 ($O=16$), hydrochloric acid must consist of 1 part by weight of hydrogen combined with 35.45 parts of chlorine.

In the electrolysis of hydrochloric acid sticks of charcoal are ordinarily used, because platinum, the substance employed in most other electrolyses, is attacked by chlorine. The apparatus of Fig. 11 is also impracticable, since the solubility of chlorine in water increases with rising pressure more rapidly than that of hydrogen, and equal volumes of both gases are therefore not obtained. In its place we use an apparatus suggested by Lothar Meyer (Fig. 15), by which the compression of the chlorine by a steadily rising column of liquid is avoided. In *A* hydrochloric acid is electrolyzed and the hydrogen and chlorine are collected in the cylinders *BB*, which are filled with a saturated sodium chloride solution. The collected gases are thus under diminished pressure.

The combination of equal volumes of chlorine and hydrogen can be carried out in a thick-walled tube, that is filled with the gases and then exposed for a day to diffused sunlight. Since the success of the experiment requires the use of the exact proportions of chlorine and hydrogen and their absolute purity, the gas mixture is prepared by electrolysis in the dark and exposed to the action of light immediately after the tube is filled.

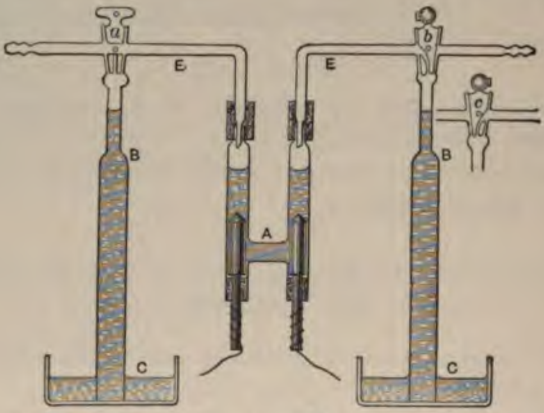

FIG. 15.—ELECTROLYSIS OF HYDROCHLORIC ACID.

The fact that hydrochloric acid gas yields a volume of hydrogen equal to half its own volume can also be shown in another way. When perfectly dry hydrogen chloride is treated with sodium amalgam—a solution of sodium in mercury—the sodium combines with the chlorine, setting hydrogen free. The volume of the latter is then found to be half as large as that of the hydrochloric acid taken.

Hydrogen and chlorine thus unite in a very simple ratio by volume (1:1), and the volume of their product also bears a very simple ratio to that of the components (2:1:1). In discussing the composition of water (§ 19) we already remarked that oxygen and hydrogen combine in a very simple ratio by volume, viz., 1:2. By carrying out this synthesis at a temperature above 100°, so that the steam is not condensed to water, it is found, further, that the volume of resulting steam bears a simple ratio to the volumes of its components, viz., that 1 vol. O + 2 vols. H gives 2 vols. H_2O.

The following arrangement serves this purpose (Fig. 16). The explosive mixture is introduced into the closed arm *B* of the U-tube over mercury. *B* is surrounded by a glass jacket, through which the vapor of boiling amyl alcohol (generated in *A*), whose temperature is about 130°, is passing. This vapor is condensed in *C*. As soon as the gas mixture has reached this temperature an induction spark is flashed through, and it is found that the volume of steam formed is two-thirds that of the mixture.

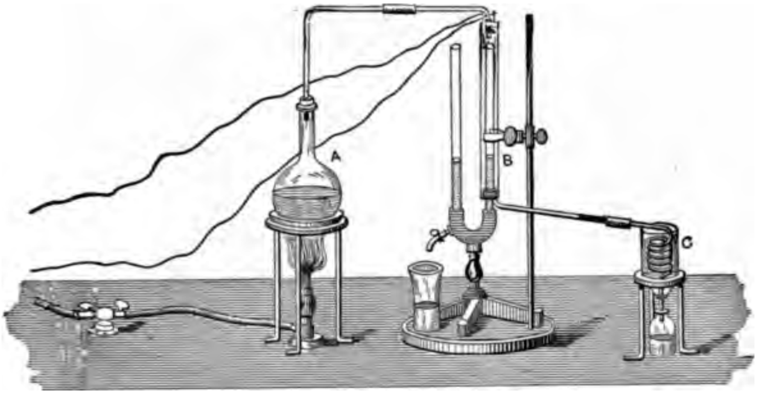

FIG. 16.—DETERMINATION OF THE VOLUME RELATIONS BETWEEN STEAM AND ITS COMPONENTS.

What was found above to be true for hydrochloric acid and for water is a general principle. *Gaseous elements combine in simple proportions by volume, and the volume of the products formed—in the gaseous state—also bears a simple ratio to the volumes of the components.* This law was discovered by GAY-LUSSAC in 1808.

This law, together with the atomic theory of DALTON, leads to important conclusions. In order to investigate the matter, let us assume that the formula of hydrochloric acid is HCl; in other words, that an atom of hydrogen is in combination with an atom of chlorine. Since one volume of hydrogen unites with one volume of chlorine to form the compound, it follows from the above assumption that equal volumes of chlorine and hydrogen contain the same number of atoms.

If the formula were otherwise, e.g. H_nCl_m, the numbers of atoms in equal volumes of hydrogen and chlorine would be in the ratio of $n:m$.

In the synthesis of water 2 vols. of hydrogen and 1 vol. of oxygen yield 2 vols. of steam. If the formula of water be $H_{2n}O_p$, the numbers of atoms in equal volumes of hydrogen and oxygen must bear to each other the ratio $n:p$.

Given, therefore, the relative numbers of atoms in equal gas volumes and the volume ratio in which the gases unite, we can determine the formula of the resulting compound.

As to the number of atoms in equal gas volumes, there was at first much uncertainty. Since all gases behave exactly alike towards changes of pressure or temperature, it was reasonable to suppose that the number should be alike for all gases; but this was soon shown to be incorrect. In the synthesis of water 3 vols. (2 vols. H + 1 vol. O) give 2 vols. of steam; hence the number of atoms per unit volume must be different for steam than for the uncombined elements. However, all difficulties were overcome by a hypothesis, which AVOGADRO enunciated in 1811, to the effect that *equal volumes of all gases at the same temperature and pressure contain the same number of* **molecules.**

AVOGADRO further supposes that the molecules of oxygen, hydrogen, chlorine, and other elements consist of two atoms. The union of hydrogen and chlorine is then explained thus: Out of a molecule of each, two molecules of hydrochloric acid are formed:

$$\underset{\text{1 vol.}}{H_2}+\underset{\text{1 vol.}}{Cl_2}=\underset{\text{2 vols.}}{2HCl}.$$

The total number of molecules thus remains the same after the combination and, since the entire volume has suffered no change either, there must be just as many molecules present in each of the two volumes of hydrochloric acid as in each of the volumes of hydrogen and chlorine.

The combination of hydrogen and oxygen takes place thus:

$$\underset{\text{2 vols.}}{2H_2}+\underset{\text{1 vol.}}{O_2}=\underset{\text{2 vols.}}{2H_2O}.$$

Every molecule of oxygen has split up into its two atoms, and each of these unites with two hydrogen atoms. The number of water molecules becomes therefore twice as great as that of the oxygen molecules and equal to that of the hydrogen molecules; but, since the volume of steam is also double that of oxygen, there must be in equal volumes just as many water molecules as oxygen molecules and hydrogen molecules.

32. It follows from the above that AVOGADRO's hypothesis is of importance in two respects: (1) in furnishing us a means of ascertaining the relative weights of the molecules of gaseous substances; (2) in putting us in a position to form an idea of how many atoms there are in the molecules.

Let us examine both points more closely. As to (1): Since equal volumes of gases under the same conditions contain the same number of *molecules*, the ratio of the weights of these volumes gives us at once the ratio of the **molecular weights.** If the specific gravity of steam is 9, based on $H=1$, and that of hydrochloric acid is 18.25, the ratio of the molecular weights of water and hydrochloric acid is 9:18.25. The determination of the specific gravity of gases and vapors, the **vapor density,** becomes therefore of the greatest importance to chemistry. The practical method of procedure is described in ORG. CHEM., § 12.

As to (2): In order to understand how AVOGADRO's hypothesis can furnish an idea of the number of atoms which the molecules of elements and of compounds contain, let us return to the example of the synthesis of hydrochloric acid. 1 vol. hydrogen unites with 1 vol. chlorine to form 2 vols. hydrochloric acid. According to the above law there must be just as many molecules present in the two volumes of hydrochloric acid as there were molecules of hydrogen and chlorine together. It is evident that this is only possible in case the molecules of hydrogen and of chlorine divide into two parts. For, if the chlorine and the hydrogen molecules consisted of only one atom each, the volume of hydrochloric acid could not, in accordance with AVOGADRO's law, be double that of each of its elements, but would have to be equal to it. It therefore follows that an even number of atoms must be present in the chlorine and in the hydrogen molecules; whether or not this number is two, as AVOGADRO assumed, can evidently not yet be determined; we shall therefore represent the molecules of hydrogen and of chlorine by H_{2x} and Cl_{2y}. From the synthesis of water the same conclusion is reached in regard to the oxygen molecule: 2 vols. hydrogen unite with 1 vol. oxygen to form 2 vols. steam. In each of these two volumes of steam there must be, according to AVOGADRO's law, just as many molecules present as in the one volume of oxygen. This is likewise impossible unless the oxygen molecule splits into two parts, each of which combines with a molecule of hydrogen, so that we obtain $H_{2x}O_z$ as the formula of water and O_{2z} as that of the oxygen molecule.

33. The formulæ for hydrochloric acid, for water and for the molecules of hydrogen, chlorine and oxygen can be fully established, if the values x, y and z are known. These can be ascertained generally in the following way: x must be at least equal to 1; if this is the case, the molecule of hydrogen becomes H_2. That a smaller number of atoms is impossible is shown by the synthesis of hydrochloric acid. The vapor densities of a series of hydrogen compounds, as compared with that of hydrogen, are then determined, from which we can find their molecular weights, based on the hydrogen molecule as unity. Thereupon these compounds are analyzed and the amount of hydrogen calculated that is represented in the different molecular weights. It will then be found that in no case is the amount less than half of that in a molecule of hydrogen. The following table gives some examples:

Substance.	Sp. G. (H = 1).	Quantity of H.
Hydrogen chloride	18.25	0.5
Hydrogen bromide	40.5	0.5
Hydrogen sulphide	17	1
Ammonia gas	8.5	1.5
Methane	8	2
Ethylene	14	2
Water	9	0.5

Since, therefore, no compound contains less than half a molecule of hydrogen, the atomic weight of hydrogen must be half its molecular weight, i.e. the formula of the hydrogen molecule is H_2. Similarly it is found that the oxygen molecule is O_2, that of chlorine Cl_2; in other words, that x, y, and z are all equal to 1. The following table illustrates the case of oxygen:

Substance.	Sp. G. (H = 1).	Quantity of O.
Oxygen	16	16
Water	9	8
Sulphur dioxide	32	16
Nitric oxide	15	8
Carbon monoxide	14	8
Carbon dioxide	22	16

RULES FOR DETERMINING MOLECULAR AND ATOMIC WEIGHTS.

34. When the atomic weight of hydrogen is taken as unity, its molecular weight is 2. If the specific gravity of another gas based on hydrogen is a, its molecules weigh a times as much as those of hydrogen, so that the molecular weight of this gas becomes $2a$. The following rule has therefore been prescribed for the **determination of the molecular weight.** *Determine the vapor density of the compound, based on hydrogen, and multiply the result by 2; the product is the molecular weight.*

For determining the **atomic weight** the following holds good, according to § 33: *Determine the composition of molecular amounts of as many compounds of the element as possible; the smallest amount of the element that is found in any instance is the atomic weight.*

[Now that molecular weights are based on $O_2=32$ ($H_2=2.016$, accordingly), the above rule, formerly exact, for determining molecular weights has become only a handy rule for approximate results. The careful student will follow the simple and fundamental rule that the ratio of molecular weights is equal to the ratio of gas densities (§ 32) and will note that the molecular weight of a substance is 32 times the quotient of the vapor density of the substance divided by the density of oxygen.]

35. AVOGADRO's hypothesis has been confirmed from a physical standpoint. It is at present one of the principal laws of chemistry and physics. Let us briefly examine, among others, the physical arguments in its favor. The molecules of bodies, solids as well as liquids and gases, are in constant motion, the intensity of which increases and decreases with the temperature. In different substances at the same temperature there must be a definite relation between the intensities of the molecular movements. This relation has been successfully worked out from the theory in the case of gaseous substances (§ 22, 3). It has been shown that in all gases at the same temperature the mean kinetic energy of translation of a molecule is the same.

The pressure which a gas exerts against the walls of the vessel is caused by the impact of the molecules. We will call the number of molecules in a volume of the gas n, the mass of each molecule m and their mean velocity u. It is then clear that the gas pressure—the above explanation of its cause being accepted—must be proportional to n and m. Moreover the pressure must also be proportional to u^2, for if the velocity were increased the enclosing walls would receive more impacts from the molecules moving to and fro, and every impact would also become stronger. The gas pressure p is therefore proportional to the product nmu^2; the theory says that $p=\frac{1}{3}nmu^2$, or $n=\frac{3p}{mu^2}$.

In this expression mu^2 is twice the kinetic energy of translation of molecules, which is the same for all gases at the same temperature. If then p is made the same for the different gases, $\frac{3p}{mu^2}$, or n, the number of molecules per unit volume, must be the same for all gases.

The laws of Boyle, Gay-Lussac and Avogadro (we refer to the expansion law of Gay-Lussac) can be expressed in a single comprehensive formula, which is worthy of note because of its frequent use in physical chemistry. The laws of Boyle and Gay-Lussac are represented by the equation

$$PV=RT, \quad \text{or} \quad \frac{PV}{T}=R,$$

in which P is the pressure, V the volume and T the absolute temperature, of the gas and R is a constant which depends on the quantity and the nature of the gas under consideration. The value of R, however, becomes the same for all gases, if molecular amounts of them (one mole each) are taken. For, according to Avogadro's law, the volume of one mole of every gas is the same under the same pressure and temperature. In the above equation, then, V is constant for all gases and, since we have already made P and T the same in each case, it is evident that R must have a constant value. In other words, if we deal with molecular amounts, the equation $PV=RT$ becomes a general expression of the laws of Boyle, Gay-Lussac and Avogadro.

The value of R may be calculated as follows: Let us consider 1 mole oxygen at 0° and 760 mm. pressure. Since 1 l. oxygen under these conditions weighs 1.4290 g., the volume V of 1 mol is

$$V=\frac{32}{1.4290}=22.393 \text{ l.}=22393 \text{ c.c.}$$

If a correction is applied because oxygen does not exactly follow the gas laws of Boyle and Gay-Lussac, we obtain 22412 c.c.

The pressure of 760 mm. mercury corresponds to a pressure of 1013.25 g. per sq. cm., i.e. $P = 1013.25$. At 0° the absolute temperature is 273° (more strictly 273.09°). Substituting these values in the above expression for R, we obtain

$$R = \frac{PV}{T} = \frac{1013.25 \times 22412}{273.09} = 83155$$

in c.-g. units. If the pressure is expressed in millimeters of mercury, R becomes

$$R = \frac{760 \times 22412}{273.09} = 62313.$$

The product PV also represents the external work which is done when a gas under constant pressure P increases its volume by V (on being heated, for instance) or when a gas being generated under the pressure P comes to occupy a volume V. For, if we suppose that the gas is enclosed in a cylinder of 1 sq. cm. transverse section having at one of its ends a piston, the increase of the volume must cause a weight P to move through V cm. One calorie (gram-calorie) = 41890 gram centimeters. If this is substituted in the equation $PV = 83155T$, the latter becomes $PV = \frac{83155}{41890}T$, or, very approximately, $PV = 2T$. This latter form also is a common one of expressing the combined gas laws. It gives the external work in calories that is done when 1 gram molecule of any given substance is converted into the gaseous state at the absolute temperature T.

Since 1 gram molecule of a gas has a volume of 22.4 l. at 0° and 760 mm. pressure, 1 c.c. under these same conditions contains $\frac{1}{22.4}$, or 0.0446, millimoles.

OZONE.

36. As early as 1785 van Marum observed that when an electric spark passes through oxygen a peculiar "garlic-like" odor is given off, and a bright mercury surface is at once made dull. Schönbein investigated this phenomenon more carefully, and found that it is due to the formation of a peculiar substance, which he called *ozone*. This proved to be oxygen existing in a peculiar condition. The fact that it really consists of nothing but oxygen is shown by its formation from perfectly dry oxygen under the influence of electric discharges, e.g. induction sparks. The amount of ozone thus formed is nevertheless small. It is greater when silent discharges are used. As ozone is formed from oxygen by ultraviolet light, the formation of ozone by silent discharges may be caused by the ultraviolet light accompanying them. This is one of the best ways of obtaining ozone; at most, however, it yields only 5.6%. Fig. 17 represents the apparatus constructed for this purpose by BERTHELOT.

The wide tube *f*, together with the supply-tube *d* and the exit-tube *e*, are sunk in a vessel of sulphuric acid, into which the pole of the inductor, *b*, is dipped. The other wire *a* of the latter ends in a tube *c*, which is slipped down inside *f* and is almost entirely filled. The silent discharge between the two bodies of sulphuric acid thus passes through a thin layer of oxygen and has a powerful ozonizing effect.

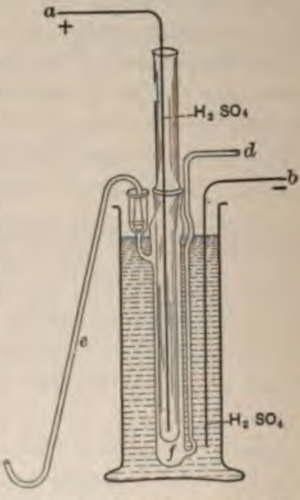

FIG. 17.—PREPARATION OF OZONE.

GOLDSTEIN obtained ozone of 100%, i.e. perfectly pure, by introducing pure oxygen in a glass tube under a pressure of 50–100 mm. and then passing through it the discharge of an induction-coil in the same manner as in a PLÜCKER tube (§ 263). When the tube was dipped in liquid air it very soon became coated on the inside with a dark blue liquid layer and the pressure fell to about 0.1 mm. The tube was then connected with a vacuum-pump, but the pressure was unaffected and remained constant so long as the liquid layer lasted, proving that this 0.1 mm. was the vapor pressure of pure liquid ozone at that temperature and not of unchanged oxygen still remaining in the tube.

Ozone is formed in many reactions, such as the slow oxidation of moist phosphorus; also in a small quantity, when hydrogen burns in an atmosphere of oxygen. The oxygen that is obtained by the electrolysis of dilute sulphuric acid always contains it. Ozone is also given off by the decomposition of permanganic acid that is set free in the reaction of potassium permanganate and concentrated sulphuric acid (*cf.* also § 52).

When oxygen is subjected to a very high temperature (e. g. flame temperature) it is partially converted into ozone, and the more so the higher the temperature (§ 103). It is necessary, however, to cool down the ozonized gas very rapidly, because the velocity of decomposition of ozone is very great, especially at high temperatures. An instantaneous cooling can be accomplished by directing the flame (of hydrogen, carbon monoxide, acetylene or other gas) upon the surface of liquid air, which has a temperature of − 180°. That the generation of ozone has no connection with the combustion, but that it is caused only by the high temperature to which the oxygen is raised by the flame, may be proved by the fact that an incandescent platinum wire or NERNST glower (§ 291), dipped in liquid air also generates ozone. The formation of ozone is also observed when a rapid current of dry air or oxygen is allowed to impinge against a hot NERNST glower. When the air contains moisture almost no ozone is formed, the product being hydrogen peroxide (§ 54).

Physical Properties.—At ordinary temperatures ozone is a gas of a peculiar odor, which is one of the most delicate tests for its presence. One part of ozone can still be detected by its odor in 500,000 parts of air. In thick layers it has a bluish color. By compressing it (slowly, to avoid warming) at a low temperature, or by cooling it through the evaporation of liquid oxygen, it can be condensed to an indigo-blue liquid, which can be separated fairly well from the more volatile oxygen by fractional distillation. Ozone boils under normal pressure at − 119°.

Chemical Properties.—Ozone is characterized above all by its ability to oxidize vigorously at ordinary temperatures, especially in the presence of moisture. Phosphorus, sulphur, and arsenic are oxidized to phosphoric acid, sulphuric acid, and arsenic acid, respectively, ammonia to nitric acid, and silver and lead to peroxides; e.g. the metallic surface of silver, especially when heated to about 240°, becomes blue when ozonized air is directed against it. Iodine is deposited by ozone from a solution of potassium iodide.

Organic substances are strongly oxidized by ozone, hence no apparatus containing it should have connections of rubber. Dye-stuff solutions, like indigo and litmus, are decolorized (by oxidation). Ozone effectively destroys micro-organisms, and is therefore used successfully in the sterilization of drinking-water.

The detection of ozone, especially in quantities too small to be recognized by the odor, is a difficult matter because several other oxidizing substances, such as chlorine or bromine in the presence of water, the oxides of nitrogen, hydrogen peroxide and still others, give closely analogous reactions and furthermore, their smell at high dilutions somewhat resembles that of ozone; hence it becomes necessary to first prove their absence. The tests for ozone are usually executed by moistening strips of filter-paper with the reagent and dipping them in the gas containing ozone. The reagents used for this purpose are lead sulphide and thallous hydroxide. The strips of paper are first moistened with dilute solutions of the nitrates of these metals and then exposed to hydrogen sulphide and ammonia fumes, respectively. Lead sulphide is oxidized by ozone to lead sulphate, thus turning from black to white; thallous hydroxide, which is white, is converted to brown thallic hydroxide. However, these changes of color also occur with the other oxidizing agents mentioned. A strictly characteristic test for ozone is the violet color produced with an acetic acid solution of tetramethyl-*p-p'*- diamido-diphenyl-methane (an organic compound.) Nitrogen dioxide gives a straw-yellow color, chlorine and bromine a dark blue, while hydrogen peroxide produces no coloration at all.

Ozone is stable at ordinary temperatures, but is easily changed to oxygen on heating. It is slightly soluble in water.

37. *Formula of Ozone.*—The formula of ozone has been determined by LADENBURG in the following way. A glass globe with two cocks was first weighed when filled with pure oxygen and then when containing ozonized oxygen. After reducing both weights to the normal temperature and pressure the globe in the latter case was found to be a mg. heavier. This increase of weight is due to the replacement of a certain number of oxygen molecules by the same number of ozone molecules.

The volume that the ozone occupies in the gas mixture can be determined by absorbing it in turpentine. Suppose this to be v c.c., when reduced to normal pressure and temperature. The weight of this v. c.c. ozone can be represented by the weight of an equal volume of oxygen $+ a$ mg. and must be, therefore, $(v \times 1.43 + a)$

mg., 1.43 mg. being the weight of 1 c.c. oxygen at normal pressure and temperature. Hence the weight g of 1 c.c. ozone is

$$g=\frac{v\times 1.43+a}{v}.$$

In one of his experiments LADENBURG found $a=16.3$ mg. and $v=26.0$ c.c., hence $g=2.06$ mg. 1 c.c. ozone thus weighs $\frac{2.06}{1.43}=$ 1.45 times as much as an equal volume of oxygen, or very nearly 1½ times as much. The molecule of oxygen being O_2, that of ozone must be represented by O_3.

In an oxidation by ozone the volume of the ozoniferous gas remains unchanged. Only the third atom in O_3 has oxidizing power, not all three atoms of the molecule.

In ozone we have become acquainted with oxygen that is different from the ordinary kind. This phenomenon is also seen in other elements; it is called **allotropism.**

HYDROGEN PEROXIDE, H_2O_2.

38. This compound is usually prepared by treating barium peroxide with dilute sulphuric acid:

$$\underset{\text{Barium peroxide.}}{BaO_2}+H_2SO_4=\underset{\text{Insoluble.}}{BaSO_4}+H_2O_2.$$

In a very concentrated state it can be obtained by direct distillation *in vacuo* of a mixture of sodium peroxide and sulphuric acid:

$$Na_2O_2+H_2SO_4=Na_2SO_4+H_2O_2.$$

Hydrogen peroxide is also formed in many other ways; e.g. together with ozone (§ 36) in the slow oxidation of phosphorus; by the combustion of hydrogen, when the flame is cooled by a piece of ice. The formation of ozone has been often detected when hydrogen in the nascent state comes in contact with oxygen molecules. We suppose that in the moment just after hydrogen is set free, its atoms have not yet united to form molecules, so that the individual atoms possess unusual chemical activity. This is the general conception of the *status nascendi*. Thus TRAUBE has observed the following instances of the production of hydrogen peroxide: Zinc filings, when shaken with water and oxygen or air, give hydrogen peroxide. since the zinc and the water generate a small quantity of hydrogen, which unites with the oxygen. Palladium-hydrogen behaves likewise when brought in contact with water and air. In this case it is the hydrogen released from the palladium that unites with the oxygen. Many metals, such as copper, lead and iron, yield hydrogen peroxide on being shaken with air and dilute sulphuric acid, for the same reason as in the case of zinc and water. Finally, the peroxide is formed in the electrolysis of water, when a current of air or, better, oxygen passes over the negative electrode (at which hydrogen is evolved).

Hydrogen peroxide is also formed at very high temperatures from water and oxygen (§ 103); just as in the formation of ozone under the same conditions (§ 36),a rapid cooling is necessary in this case also, else the compound decomposes. The formation of hydrogen peroxide in the combustion of hydrogen has been shown in the following way: A hydrogen flame was allowed to burn at the mouth of a bulb tube containing a little water. By means of a very rapid current of air the flame was blown into the bulb, causing a very sudden cooling of the mixture of steam and air. After a time the water in the bulb gave the tests for hydrogen peroxide. As a further analogy to the case of ozone it has been shown that the formation of hydrogen peroxide has no connection with the combustion, for on directing a fine stream of water upon an incandescent NERNST glower some hydrogen peroxide is generated in the water.

Physical Properties.—In the pure anhydrous condition hydrogen peroxide is a colorless, slightly viscid liquid, having a specific gravity of 1.4584 at 0°, based on water at 4°. (A density calculated on this basis is indicated by $d_4°$.) It becomes solid at a low temperature and melts at $-2°$.

Chemical Properties.—Hydrogen peroxide, when wholly free from impurities, especially from suspended particles of solid matter, is rather stable and can be distilled *in vacuo;* when impure, it decomposes, however, into water and oxygen, as it also does in dilute solution. In the latter state it is more stable in the presence of traces of acid than in the presence of bases. It is an interesting fact that it decomposes rapidly in contact with powdered substances, apparently without acting upon them. Finely divided silver, gold, platinum (platinum black), and especially manganese dioxide decompose it with effervescence (due to escaping oxygen). Even rough surfaces have a disturbing effect; BRÜHL observed, for instance, that a concentrated solution of hydrogen peroxide evolves oxygen when poured upon ground glass. All these actions must be regarded as catalytic accelerations of the ordinarily very slow decomposition of hydrogen peroxide. The effect of heat is here, as elsewhere, to accelerate the reaction; concentrated preparations, when warmed, often decompose so rapidly as to cause an explosion.

The *oxidizing action* of hydrogen peroxide is an important chemical property. This is always due to the surrender of an oxygen atom, which effects the oxidation, while water remains. Lead sulphide, PbS, is oxidized by a weak solution of hydrogen peroxide to lead sulphate, $PbSO_4$; sulphuretted hydrogen, H_2S, is converted into water and free sulphur. Barium, strontium and calcium hydroxides, $Ba(OH)_2$, $Sr(OH)_2$ and $Ca(OH)_2$, are precipitated by dilute hydrogen peroxide from their solutions as peroxides of the general formula $MO_2 \cdot n\text{aq}$.[1] The colorless solution of titanium dioxide in dilute sulphuric acid is turned orange-red by hydrogen peroxide—lemon-yellow by traces of it —on account of the formation of yellow trioxide, TiO_3. This is a delicate *test for hydrogen peroxide.* Other tests are found in the following oxidation reactions: Potassium iodide starch-paste is at once turned blue by hydrogen peroxide in the presence of a little ferrous sulphate, $FeSO_4$.

The ferrous sulphate carries the active oxygen of the hydrogen peroxide to the potassium iodide. As a result two atoms of iodine are set free, the ferrous sulphate being oxidized at the same time. According to MANCHOT a higher oxide of iron is formed in this reaction.

A very characteristic reaction is this: Chromic acid solution (H_2CrO_4), when treated with hydrogen peroxide, is changed to a higher oxide (see § 295) which is blue in aqueous solution and may be taken up by ether if shaken with the latter. This test is, however, less delicate than the two preceding ones.

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[1] Aq. (*aqua*), a frequently used abbreviation for water of crystallization or hydration.

A third group of chemical effects of hydrogen peroxide depends on its *reducing power*. When silver oxide is introduced into a solution of hydrogen peroxide, a vigorous evolution of oxygen occurs, water and metallic silver being formed at the same time. Potassium permanganate solution loses its color when mixed with a hydrogen peroxide solution acidulated by sulphuric acid, oxygen being given off rapidly:

$$2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+8H_2O+5O_2.$$

The brown peroxide of lead, PbO_2, is reduced to reddish-yellow lead oxide, PbO.

Ozone and hydrogen peroxide yield water and oxygen; when dilute, they are, however, able to exist side by side.

There is a test for hydrogen peroxide, depending on its reducing power, which is even more delicate than those described above. A mixed solution of ferric chloride and red prussiate of potash has a red color. On the addition of hydrogen peroxide Prussian blue is precipitated. Traces of the peroxide turn the solution green. The reaction fails in the presence of free acid.

The ability of so powerfully oxidizing a substance as hydrogen peroxide to act also as a reducing-agent can be explained as follows: One of its two oxygen atoms must be loosely joined to the molecule, since it is easily given up. All the substances which are reduced by hydrogen peroxide, also have one loosely held oxygen atom; silver oxide, potassium permanganate, ozone and others give up their oxygen at rather low temperatures. It is therefore possible that the mutual attraction of the oxygen atoms, which tends to make them form oxygen molecules, is stronger than the force by which they are held in hydrogen peroxide on the one hand, and the respective oxygen compound on the other.

Uses of Hydrogen Peroxide.—The colors of old paintings are often restored by means of it. The darkening of them is due in many cases to the transformation of white lead sulphate, $PbSO_4$, to black lead sulphide. The latter is readily oxidized by hydrogen peroxide back to white lead sulphate. Hydrogen peroxide is also of value in bleaching ivory, silk, feathers, hair, bristles and sponges. It is also important in analysis.

For therapeutic purposes at 30% solution of hydrogen peroxide is prepared by MERCK which is perfectly pure and is obtained by vacuum distillation from a more dilute solution. Before use it is strongly diluted. It has the advantage of not being subject to decomposition. The concentration of a solution of hydrogen peroxide is generally expressed in the volumes of oxygen that it can evolve; thus, for a 3% solution it is ten volumes.

39. The *composition* of hydrogen peroxide was established by THÉNARD as early as 1818. He first concentrated it in a vacuum and then introduced a weighed amount of it, enclosed in a vial, into a graduated barometer-tube over mercury. The vial was then broken and its contents decomposed by heating the tube from without or allowing finely powdered manganese dioxide to rise in the tube. It was thus found that very nearly 17 parts of hydrogen peroxide by weight yield 8 parts of oxygen, water being also formed. One atom of oxygen (16 parts by weight) is therefore obtained from 34 parts of hydrogen peroxide, the remaining 18 parts forming water; in other words, hydrogen peroxide is 1 molecule $H_2O + 1$ atom O. The peroxide therefore contains one atom of oxygen to every hydrogen atom. Its simplest formula (the so-called *empirical formula*) is then HO. Whether this also expresses the molecule or whether the latter is a multiple of it, remains to be determined by finding the molecular weight, inasmuch as every compound of the general formula $(HO)_n$ possesses the same composition, viz., 16 parts by weight of oxygen to 1 part of hydrogen.

On account of the instability of this substance its vapor density cannot well be determined. It was therefore necessary, in finding its molecular weight, to follow another course, which is based on the properties of dilute solutions. In this manner the molecule of hydrogen peroxide was found to possess the formula H_2O_2. The method referred to is explained in the following sections.

MOLECULAR WEIGHT FROM THE MEASUREMENT OF THE DEPRESSION OF THE FREEZING-POINT AND ELEVATION OF THE BOILING-POINT.

40. Certain membranes possess the peculiar property of allowing a solvent, e.g. water, to pass through, but not the dissolved substances. They bear the name "*semi-permeable membranes.*" This property appears to depend not so much on a sort of sieve action as upon the ability of the membrane to dissolve, or else to absorb or loosely combine with, the solvent on one side and release it again on the other, while the dissolved matter remains behind. One of the ways of obtaining a semi-permeable partition is by dipping a porous cup—such as is used in galvanic cells—containing a solution of yellow prussiate of potash into a solution of blue vitriol. A thin layer of copper ferrocyanide is thus formed in the wall of the cup, making it semi-permeable. If a dilute sugar solution, salt solution or the like be poured into such a cup and the cup placed in a dish of water, it will be found that the dissolved substance does not diffuse through this sort of a partition. The water goes through, however, for if the cup be closed with a perforated stopper through which a glass tube passes and then dipped deep enough under water so that the entire cup is submerged, the water will be seen to rise slowly in the tube till it reaches a definite height above the level outside.

The pressure exerted by this column of liquid is called the *osmotic pressure* of the solution. If a tight-fitting piston were inserted in the cup, the force which one would have to exert on it to prevent the infiltration of the water would be equal to the pressure of the column of liquid, for the water continues to rise in the tube till the pressure of the column prevents the entrance of any more.

According to researches of VAN'T HOFF the osmotic pressure of dilute solutions, like the pressure of gases, obeys the law of BOYLE and the expansion law of GAY-LUSSAC. If the pressure exerted at a certain temperature by a kg. of a gas in a vessel be p, the pressure which na kg. of the gas at the same temperature exerts in the same vessel is np. The *concentration*, i.e. density, of the gas has been multiplied n-fold.

If the osmotic pressure of a solution containing a per cent of a substance be determined and found to be p, the osmotic pressure will be np, if an na per cent solution of the same temperature be taken, i.e. if the concentration be n times as great.

An investigation of the pressures which a gas of constant volume exerts at the absolute temperatures T_1 and T_2 shows that these pressures bear to each other the ratio $T_1 : T_2$. The same proportion is observed when the osmotic pressure of a solution of constant concentration is measured at the same absolute temperatures as above.

41. The laws of osmotic pressure find experimental verification in measurements which were made by PFEFFER previous to VAN'T HOFF'S enunciation of the laws. PFEFFER investigated dilute sugar solutions and used an apparatus not unlike the one just described.

The gas laws are expressed by the equation

$$PV = RT, \quad \dots\dots\dots \quad (1)$$

in which P represents the pressure, V the volume, and T the absolute temperature of a gas, while R is a constant. The volume, V, is inversely proportional to the concentration, according to the above definition; therefore $\frac{1}{C}$ may be substituted for V, if C indicates the concentration. The above equation then becomes

$$\frac{P}{C} = RT,$$

or, at a constant temperature,

$$\frac{P}{C} = \text{Const.}$$

This equation must also be applicable to osmotic pressure. This was really the case in PFEFFER'S measurements of aqueous sugar solutions of different concentrations, as may be seen from the following brief table. The temperature varied between 13.5° and 16.1°, and hence was not perfectly constant:

C.	P.	$\frac{P}{C}$
1%	535 mm.	535
2%	1016 "	508
4%	2082 "	521
6%	3075 "	513

The differences in the values of $\frac{P}{C}$ must be ascribed to the variations of temperature and the unusual experimental difficulties which attend such measurements.

From equation (1) it also follows, when V (or C) is a constant, that

$$\frac{P}{T} = \text{Const.}$$

This conclusion, too, was demonstrated experimentally by Pfeffer in the case of sugar solution, as may be seen from the following table. A one per cent solution was used:

P.	T.	$\frac{P}{T}$
510	287.15	1.78
520.5	288.5	1.80
544	305	1.78
567	309	1.83

Van't Hoff has further shown that the numerical value of the osmotic pressure is the same as that of the gas pressure; that is to say, when a definite amount of a substance in the gaseous state occupies a given volume, the gas pressure which it exerts is just as great as the osmotic pressure which would be produced if the same amount of substance were dissolved in a liquid making the same volume of solution.

The measurements of Pfeffer also furnished experimental proof of this. He found that a 1% sugar solution at 7° exerts a pressure of $\frac{2}{3}$ of an atmosphere. If there is really equality between osmotic pressure and gas pressure, or, in other words, if the law of Avogadro for gases is also applicable to dilute solutions, the constant R of the equation $PV=RT$ must have the same value for solutions as for gases. P in the above case was found to be $\frac{2}{3}$ of an atmosphere, or $\frac{2}{3}\times 760=506$ mm. mercury. A 1% sugar solution contains 1 g. sugar in 100.6 c.c. As the molecular weight of this substance is 342, the volume V which contains 342 g. is $V=100.6\times 342$. $T=273+7°=280°$. Substituting these figures in $R=\frac{PV}{T}$, we have $R=62313$. The close agreement of the two values of R (compare p. 50) proves the equality of gaseous and osmotic pressure.

42. It follows from the preceding that Avogadro's law must also hold for dilute solutions. Assuming that an equal number of molecules of different substances are dissolved in equal volumes at the same temperature, we know from the equality of gas pressure and osmotic pressure that the various substances will exert the same osmotic pressure; inversely, in equal volumes of solution having the same temperature and osmotic pressure there is the same number of molecules.

This is a very important extension of Avogadro's law. We are thus able not only to compare the weights of equal gas volumes at the same temperature and pressure and calculate therefrom the molecular weight, but we can apply the same principle to solutions, since we know that in solutions of the same temperature and the same osmotic pressure the quantities of the dissolved substances contained in equal volumes of solution are to each other as their molecular weights.

Just as it is possible to ascertain the molecular weights of gaseous bodies from determinations of temperature, pressure, weight and volume, it is also possible to find those of substances in dilute solution by measuring the volume of liquid, the temperature, the quantity dissolved and the *osmotic* pressure. The molecular weights of all substances that dissolve in some liquid or other can be determined in this way, and, since the number of soluble substances is very large, there are not a few whose molecular weights were first determined in this way.

In working out this method, however, there is a practical difficulty. The osmotic pressure is very hard to measure directly. This would render the whole method of little value, if it were not for the fact that the calculation only requires that it be known whether two solutions have the *same* osmotic pressure, not the absolute amount of the latter; the law of AVOGADRO simply requires the equality of volume, of temperature and of pressure (osmotic or gas), without regard for the absolute value of these factors (between certain limits). Now, it is easy to measure magnitudes which are proportional to the osmotic pressure, and from which it may be seen whether equality of osmotic pressure exists or not. These magnitudes are the **depression of the freezing-point** and the **elevation of the boiling-point.** An explanation of these terms is perhaps necessary:—When a substance is dissolved in a liquid the maximum tension of the vapor is less above the solution than above the pure solvent at the same temperature, for the particles of the dissolved body attract the molecules of the solvent, hindering the formation of vapor on the one hand, and, on the other hand, facilitating the return of vapor molecules into the liquid. This lowering of the vapor pressure necessarily causes a depression of the freezing-point and an elevation of the boiling-point, as may be proved by the following diagrams. In Fig. 18, *abc* represents the vapor-pressure curve of a solvent in the neighborhood of its freezing-point *b*; the part *ab* gives the pressures for the frozen matter; the part *bc* for the liquid solvent. This latter part is always more nearly horizontal than the former, as has been proved both experimentally and theoretically. The freezing-point of a liquid is that temperature at which the solid and liquid states can exist side by side indefinitely. This condition requires that the solid and the liquid substance have the same vapor tension. If, for instance, the vapor tension of the solid were greater than that of the liquid, we should have, at a constant temperature, the vapor given off from the solid condensing to a liquid and the former gradually turning into the latter. Inversely, if the vapor tension of the solid were less than that of the liquid, the entire liquid would, under similar conditions, solidify.

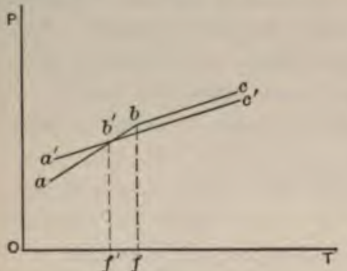


FIG. 18.

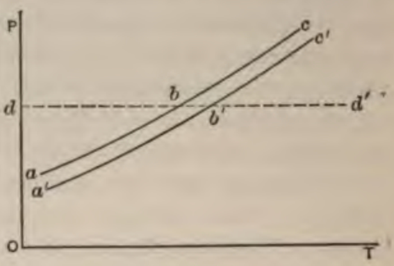


FIG. 19.

The freezing-point b can thus be regarded as the intersection of the vapor-pressure curves ab and bc of the solid and the liquid, respectively. Let us now consider the curve $b'c'$ of a solution. Its vapor pressure is lower than that of the pure solvent, so its intersection with the curve ab must lie more to the left, that is, its freezing-point is lowered. On the other hand, the boiling-point of a solution is that temperature at which the tension of its vapor equals one atmosphere. If Od in Fig. 19 represents this tension, a line dd' parallel to the axis of abscissas will intersect the vapor-pressure curve ac of the pure solvent at a lower temperature, than it will the curve $a'c'$ of the solution. The latter must, therefore, have a higher boiling-point.

43. The connection between these magnitudes and the osmotic pressure will be better understood after the following considerations:

1. *Solutions in the same solvent, separated by a semi-permeable partition, can only be in equilibrium when they are isotonic, i.e. when they exert the same osmotic pressure.*

Let us imagine the solutions in an apparatus consisting of two cylinders that are connected by a tube containing a semi-permeable partition. In both cylinders the level of liquid is kept at the same height constantly by adding or removing some from time to time.

The solution with the greater osmotic pressure will extract solvent from the other, for, because of the stronger pressure which the dissolved molecules exert upon the free surface of the liquid, the first solution will endeavor to increase in volume at the expense of the second. Equilibrium will be established so soon as the same pressure is exerted by the dissolved molecules upon the unit area of the free surfaces of the liquids from both sides of the semi-permeable partition; in other words, when the solutions are isotonic.

2. *Isotonic solutions with the same solvent have the same vapor tension at the same temperature.*

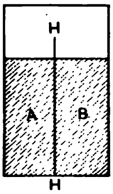


FIG. 20.

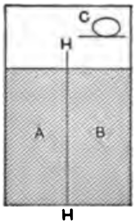


FIG. 21.

The proof of this statement lies in the contradiction to which the assumption that isotonic solutions have unequal vapor tensions leads. The accompanying diagram, Fig. 20, represents a closed vessel, that is separated by the semi-permeable partition *HH* into two parts, which contain the isotonic solutions *A* and *B*. Near the top the two parts are connected with each other. Assuming that the vapor tension of *A* is greater than that of *B*, vapor must pass out of *A* and condense in *B*; the result is that *A* becomes more concentrated, *B* more dilute, and they are no longer isotonic. In such a case, according to the first principle, the solvent would then begin to pass through *HH* from *B* to *A*. The assumption of perpetual motion which is thus made necessary can only be avoided by supposing that the vapor tension is the same.

3. *Isotonic solutions with the same solvent have the same freezing-point.*

Let us again take the same apparatus, containing, in addition to the isotonic solutions *A* and *B*, a piece, *C*, of the solvent in the solid state (Fig. 21). Let us also assume that *A* and *C* have the same vapor tension. We then have, according to definition (see § 42), the temperature of the freezing-point of A. However, if A and B are isotonic, they have the same vapor tension. B will, therefore, have the same vapor tension as C. Hence B and C must also be at their only coexistence temperature, the freezing-point of B. At their freezing-points A and B, therefore, have the same temperature as C, i.e. they possess the same freezing-point.

4. *Isotonic solutions with the same solvent have the same boiling-point.*

As we saw in § 42, the boiling-point of a solution is that temperature at which the tension of its vapor equals one atmosphere. Two solutions with a common solvent, therefore, have the same vapor tension at their boiling-point. Now, it was shown above that solutions having the same temperature and vapor tension are isotonic. If these solutions have the same vapor tension (at their boiling-point) and are isotonic, they must also have the same temperature.

Since, as has just been demonstrated, isotonism requires like freezing-points and boiling-points, it is evident the depression of the freezing-point and elevation of the boiling-point must be the same in isotonic solutions with the same solvent.

In the depression of the freezing-point and the elevation of the boiling-point we thus have a means of deciding whether solutions are isotonic. Use is made of this fact for the determination of molecular weights in the following way: The freezing-point of a liquid, e.g. water, acetic acid, phenol, etc., is first determined. Thereupon a gram molecule of a substance whose molecular weight is known is dissolved in a given weight (hence also in a given volume) of the liquid. A depression of the freezing-point is observed. This depression will always be the same, no matter what the substance is that is dissolved in the liquid, providing that one gram molecule is dissolved in the same volume of liquid. The depression of the freezing-point for one gram-molecule of solute is thus a constant for the solvent.

Now if we prepare a 1% solution of a compound whose molecular weight, M, is unknown and measure the freezing-point depression, A, we have

$$AM = \text{Constant}.$$

This formula is also applicable to the elevation of the boiling-point, as can be readily seen. M is the only unknown and can therefore be calculated.

When water is used as the solvent, the product of the depression A of the freezing-point of a 1% solution and the molecular weight M has been found from numerous observations to be 19. We have therefore for water

$$AM = 19.$$

For hydrogen peroxide, the depression of the freezing-point of a 3.3% aqueous solution was found to be 2.03°. This would correspond to $\frac{2.03}{3.3} = 0.615°$ for a 1% solution; hence $A = 0.615$, from which it follows that the molecular weight is $\frac{19}{0.615} = 30.9$.

Since the formula HO corresponds to a molecular weight of 17, H_2O_2 to one of 34, and the latter number is the nearer to the molecular weight found by experiment, we conclude that hydrogen peroxide has the doubled empirical formula H_2O_2.

The constants for the freezing-point depression (*molecular depression*) and for the elevation of the boiling-point (*molecular elevation*) of some compounds that are well adapted for these determinations are given in Org. Chem., § 13.

The freezing-point method for determining molecular weight is called the *cryoscopic method*, while the boiling-point method is known as the *ebullioscopic method.* Apparatuses for the easy and exact determination of the depression of the freezing-point and elevation of the boiling-point are described in Org. Chem., §§ 14 and 15.

BROMINE.

44. This liquid element does not occur free upon the earth because of its strong tendency to form compounds. In combination with metals it is found in the salts of sea-water. It was discovered in the latter by Balard in 1826. Bromides occur in rather large amounts in the so-called *Abraum-salze* of the Stassfurt salt-mines, and also in considerable quantities in the brines of many salt wells, notably those of Michigan.

In the neighborhood of Stassfurt, Germany, there are extensive beds of rock-salt (halite). Above the halite are found layers of other salts (called "Abraum-salze" because they have to be removed in order to get at the halite). These salts were formerly rejected as worthless, but they have since been found to be rich in potassium salts, bromides and other valuable minerals, so that the "waste salts" of former days are now the leading source of many commercially and scientifically important compounds.

The purification of these Stassfurt salts is accomplished by solution in water and partial evaporation of the latter. Various substances crystallize out, while the remaining liquid ("mother-liquor") still contains the most soluble salts, among which is magnesium bromide, $MgBr_2$. From this mother liquor the bromine is obtained by the use of chlorine, which sets bromine free from bromides, thus:

$$MBr + Cl = MCl + Br. \quad (M = \text{Metal.})$$

The process employed is an application of the principle of the counter-current (§ 15). The mother-liquor is allowed to flow down through a tower filled with round stones, so that the exposed surface of the liquid is greatly enlarged. A current of chlorine is passed into the tower from below, and, as it rises, the gas is in constant touch with the bromide liquor, the most concentrated gas being in contact with liquor which has already yielded the greater part of its bromine, so that practically all the bromine is thus easily obtained. The bromine prepared in this way always contains a little chlorine, from which it is freed by distillation over finely powdered bromide of potassium.

Another method, common in the United States, of obtaining the bromine from the mother-liquor is by distilling the latter with manganese dioxide (or potassium chlorate) and sulphuric acid, corresponding to the method of making chlorine (§ 25). Still another method is to electrolyze the bromide solution and boil off the bromine.

The bromine thus obtained still contains a little water. It is dried by shaking it with concentrated sulphuric acid and then distilling again.

Physical Properties.—Bromine is a liquid at ordinary temperatures; it is the only element, excepting mercury, that displays this property. It solidifies at −7.3° and boils at 59°. It is dark brown, and is transparent only in thin layers. At the temperature of liquid hydrogen (20.5° absolute) it becomes colorless; MOISSAN showed the same to be true of chlorine and fluorine as well. It is quite volatile at ordinary temperatures, giving off brown fumes of an extremely irritating and disagreeable odor, whence its name (*βρῶμος* = stench). Sp. g. = 3.1883 at 0°. 100 parts of water dissolve 3.5 parts of bromine. The addition of potassium bromide to the water increases its solubility a little. Its vapor density is 79.96 (O = 16).

The *chemical properties* of bromine are completely analogous to those of chlorine, but the action of the former is less energetic. While, for instance, chlorine combines with hydrogen in the daylight at ordinary temperatures, bromine does not. Its affinity for many elements is, however, very strong. It reacts vigorously with phosphorus; and powdered arsenic and antimony take fire when sprinkled upon bromine. It is an interesting fact that of the two closely related alkali metals, potassium and sodium, the former reacts vigorously with bromine, while the latter does not react with it at all at ordinary temperatures.

The *bromine molecule* consists of two atoms; for, since its vapor density is 79.96 (see above), its molecular weight must be 159.92. Inasmuch as a gram-molecule of no one of the very numerous bromine compounds contains less than 79.96 g. bromine, but often simple multiples of this quantity, its atomic weight is taken to be 79.96, based on O = 16. The molecule, therefore, contains $\frac{159.92}{79.96} = 2$ atoms.

HYDROGEN BROMIDE, or HYDROBROMIC ACID, HBr.

45. This gaseous compound can be obtained by direct synthesis from its elements; for this purpose it is necessary to pass hydrogen, together with bromine vapor, through a hot tube containing platinum gauze. This is the most practical method of manufacturing it.

Hydrobromic acid can also be obtained by the action of hydrogen on *bromine compounds*. Silver bromide, AgBr, for example, is reduced by hydrogen at a high temperature to metallic silver with the formation of hydrogen bromide.

On the other hand, it is also formed by the action of bromine on *hydrogen compounds*. For this purpose numerous organic compounds can be used. For example, bromine reacts with naphthalene, $C_{10}H_8$, at ordinary temperatures to form hydrogen bromide, somewhat impure, however, from the presence of organic substances. Hydrogen bromide is also produced, together with free sulphur, when hydrogen sulphide is led into bromine under water:

$$H_2S + Br_2 = S + 2HBr.$$

Hydrobromic acid may also be prepared by the decomposition of a bromine compound with a hydrogen compound, phosphorus pentabromide, PBr_5, and water being employed:

$$PBr_5 + 4H_2O = 5HBr + \underset{\substack{\text{Phosphoric}\\ \text{acid.}}}{H_3PO_4}.$$

As phosphoric acid is not volatile, but the desired substance is, the two products of the reaction can be easily separated.

Physical Properties.—At ordinary temperatures hydrogen bromide is a gas. It can be condensed, by cooling, to a liquid which boils at −64.9° (under 738.2 mm. pressure), and, by still farther cooling, to colorless crystals, which melt at −88.5°. It has a pungent odor and a sour taste. In contact with moist air it forms dense clouds, like hydrochloric acid (§ 29). It is very soluble in water, 1 vol. water dissolving about 600 vols. at 10°; its solubility is thus even greater than that of hydrochloric acid.

Chemical Properties.—Here, too, the acidic nature is strongly displayed. Various metals, such as zinc and magnesium, are acted upon by hydrobromic acid, forming a salt and free hydrogen. The most of its salts are soluble in water; silver bromide, however, is insoluble and lead bromide difficultly soluble.

A very high temperature is required to decompose hydrogen bromide into its elements.

The *composition of hydrobromic acid* can be determined in the same way as that of hydrochloric acid. Since its vapor density is 40.38, it has a molecular weight of 80.76. The atomic weight of bromine being 79.96 ($O = 16$), it follows that the formula of hydrobromic acid must be HBr. Moreover, the dry gas can be decomposed with sodium amalgam, whereby it is found that half of its volume consists of hydrogen; this confirms the above molecular formula.

IODINE.

46. This element, a crystalline solid, was discovered by COURTOIS in 1812, but its elementary nature was first recognized in 1815 by GAY-LUSSAC. Like chlorine and bromine, it does not occur in the free state, but is frequently found in nature in combination with some metal. An important source of iodine compounds is the mother-liquor (§ 44) remaining in the purification of Chili saltpetre; another, the ash of seaweeds, known in Scotland as *kelp* and in Normandy as *varec*, which contains iodides. The extraction of the iodine is accomplished either by passing chlorine into the solution or by distilling with manganese dioxide and sulphuric acid in the same manner as for bromine and chlorine. The commercial iodine is purified by warming it gently with the addition of a little potassium iodide, the iodine subliming in the pure state, free from traces of chlorine and bromine that may have been present. Finally, it is dried in a desiccator over sulphuric acid.

Physical Properties.—Iodine forms tabular crystals of a dark gray metallic lustre. Its specific gravity is 4.948 at 17°. It melts at 114.2°, and boils under 760 mm. pressure at 184.35°. Its vapor is characterized by a beautiful dark-blue color, which gave the element its name (*ioειδης* = violet). In water it is only slightly soluble—enough, however, to color the water yellow. It dissolves easily in a solution of potassium iodide, the latter being turned brown. In various other liquids, such as alcohol, ether, carbon disulphide and chloroform, iodine is also easily soluble. It is a peculiar fact that the alcoholic and the ethereal solutions are brown, while the solutions in carbon disulphide and chloroform are violet; other solvents, e.g. benzene, give solutions of an intermediate color. The probable explanation of this diversity of color is that in the brown solutions the iodine has formed a compound with the solvent, whereas in the violet solutions, which have very nearly the same color as iodine vapor, the element exists in the free state.

This conclusion is based on the behavior of the brown solution in water (to which some glycerine has been added to increase the solubility of the iodine) towards other solvents. According to the distribution law of BERTHELOT (ORG. CHEM., § 24) the iodine should distribute itself in a constant ratio between the two liquids when this solution in water-glycerine is shaken with a second liquid not miscible with it, i.e. the coefficient of distribution should be independent of the quantity of iodine present. In agreement with this law the distribution coefficient was found to be constant for different temperatures (as is ordinarily the case) when ether, with which iodine also forms a brown solution, was used as a second solvent; but dependent on the temperature when the ether was replaced by chloroform, in which iodine dissolves with a violet color. This can be explained by assuming that the iodine does not exist in the same state in the water as in the chloroform. Since not only iodine but other substances as well exhibit this anomalous behavior when dissolved in water (or a solvent of the same type, e.g. ether), it may be supposed that these solvents enter into combination (*associate*) with the dissolved substance.

47. The vapor density of iodine is 8.72 (air=1) at about 600°. As the temperature rises, it grows steadily smaller, however. Thus we have:

Temperature.	Vapor Density.
878°	8.11
1030°	6.83
1250°	5.65
1390°	5.23
1500°	4.5

At 1500° we see it is reduced to almost half of what it is at 600°. As we shall later (§ 49) have occasion to discuss this phenomenon, called dissociation, which has also been observed in many other substances, it will here suffice to explain how the vapor densities at such elevated temperatures have been determined by V. MEYER and his pupils.

The apparatus he employed (Fig. 22) consists of a cylinder 200 mm. deep and 36 mm. in diameter, connected with which is a 4-mm. tube 350 mm. long. There is also a capillary tube leading to the bottom of the cylinder. The entire apparatus is constructed of platinum. In determining vapor density at a high temperature the apparatus—properly protected from direct contact with the flame—is placed in a Perrot furnace in such a manner that the tube protrudes enough to attach a piece of rubber tubing, connecting the apparatus with a tube provided with a side arm for the escape of gases. The apparatus does not differ essentially from that employed in the ordinary determination of vapor density according to V. Meyer (Org. Chem., § 12). When the lower part of the apparatus has reached the temperature of the furnace the vapor density is determined in the usual way, a knowledge of the temperature being, of course, just as unnecessary as in the previous case.

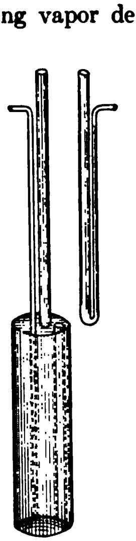


Fig. 22.—Apparatus for the Vapor-density Determination of Iodine, after V. Meyer.

Victor Meyer, however, was interested in determining not only the amount of the vapor density, but also the way in which it varies with the temperature. To this end it was, of course, necessary to know the temperature at which each measurement was made. This can be ascertained with the help of the same apparatus in the following manner: The volume of air (or nitrogen) contained by the apparatus at the ordinary temperature is measured by displacing the air with carbon dioxide, which is passed through the capillary tube to the bottom of the vessel; the air is collected in a graduated tube over a liquid (caustic potash solution) which completely absorbs the carbon dioxide. The same operation is repeated subsequently, when the apparatus is glowing hot, as soon as the vapor-density determination is completed and air has been passed through the apparatus for a few minutes in order to expel the vapor of the substance whose density has been determined. The volume of air then present in the apparatus, together with the volume contained at the ordinary (measurable) temperature and the expansion coefficient of air, furnish all the data required for a calculation of the desired temperature. There is, however, one difficulty: only the lower part of the apparatus is at the temperature to be measured; the adjoining tube and the other parts of the apparatus, such as the glass side-tube, are at a different temperature. Hence a correction must be introduced in the calculation, which is found with the help of the *compensator* (Fig. 22). This consists of two platinum tubes of exactly the same dimensions, and, therefore, the same capacity, as the two tubes which protrude from the cylinder.

To these last-named tubes the compensator is attached by means of platinum wire. It may be assumed that the air in the latter has the same temperature as that in the corresponding parts of the real apparatus. It is readily seen that, when the volume of the compensator at the ordinary temperature and that at the temperature at which the determination is made are subtracted from the corresponding volumes of the real apparatus, the remainder is the volume of air contained in the lower wider portion at the temperature of the experiment.

With the aid of an electrically heated apparatus of iridium **Nernst** has extended the possible range of this method to 2100°.

In temperature measurements of this sort the following is also to be noted: The entire method is based on the assumption that the coefficient of expansion of air stays the same at these high temperatures; in other words, that the specific gravity of air remains constant, and does not diminish, like that of iodine. This assumption was, however, hardly reliable. In order to test the matter it would be necessary to measure the volume at a known high temperature, whereas in these experiments the temperature is unknown and must be calculated from the volume. To avoid this difficulty the temperature measurement was carried out with different gases in the same manner as above. The results were the same. Now, it was very improbable that all of the gases employed (oxygen, nitrogen, carbon dioxide, sulphurous oxide and others) should show a decrease of density and all in the same measure. Therefore it was reasonable to assume that their expansion is normal.

The *chemical properties of iodine* resemble very strongly those of chlorine and bromine. Its affinity for other elements is in general weaker, however, than that of the two halogens mentioned. It combines with metals, e.g. mercury, directly to form salts (iodides). A characteristic test for iodine is the intense blue coloration which it imparts to starch solution; the slightest traces of iodine can be thus detected. The blue color disappears on boiling and reappears on cooling, provided the boiling was not too prolonged.

The *molecule of iodine*, investigated by the same method as was employed with bromine, is found to consist of two atoms at 600°, hence the formula is I_2. Above 1500° it must contain only one atom, for the vapor density is less by one-half.

HYDROGEN IODIDE, or HYDRIODIC ACID, HI.

48. This compound can be obtained by direct synthesis from its elements, and that is really the best method for preparing it in a perfectly pure state. For this purpose hydrogen and iodine vapor are conducted together over heated platinum-black, which accelerates their combination.

Hydrogen iodide can also be obtained by the reaction of iodine with hydrogen compounds. Organic hydrogen compounds are preferable, especially colophonium and copaiva oil. This method is also used for the laboratory preparation of the gas, but the hydrogen iodide thus obtained is more or less adulterated with organic substances. When iodine acts on hydrogen sulphide water hydrogen iodide is formed, sulphur being liberated (§ 45).

As an example of the action of hydrogen on an iodine compound, we may mention the reduction of silver iodide by hydrogen, from which hydrogen iodide results.

Finally, the action of an iodide on a hydrogen compound is illustrated by the decomposition of a phosphorus iodide, PI_3 or PI_5, by water. As was explained in § 45, it is possible to use phosphorus, iodine and water. This method, with some variation or other, is the preferable one for the preparation of hydriodic acid.

According to Gattermann, it is best to first add yellow phosphorus (4 g.) in very small pieces to 44 g. iodine, and then decompose the resulting compound with a little water. In order to remove the free iodine from the hydrogen iodide formed, the gas is allowed to pass over red phosphorus.

The decomposition of the halogen salt by sulphuric acid is even less available for the preparation of hydriodic than for hydrobromic acid, since the former is more easily decomposed by sulphuric acid than the latter.

Physical Properties.—Hydrogen iodide is a colorless gas, whose specific gravity is 62.94 ($H = 1$). It fumes strongly when exposed to the air, and possesses an acid reaction and a pungent odor. At 0° and 4 atmospheres pressure it condenses to a colorless liquid, which boils at $-34.14°$ under a pressure of 730.4 mm. The melting-point of the solid is $-50.8°$. Hydrogen iodide is very soluble in water; 1 vol. H_2O at 10° dissolves 425 vols. HI. This solution fumes strongly, and turns dark brown after a time, because of the liberation of iodine.

Chemical Properties.—Hydrogen iodide has all the characteristics of an acid. With metals it forms salts (iodides), hydrogen being given off. These are almost all soluble, with the exception of the iodides of silver and mercury. Lead iodide is slightly soluble at ordinary temperatures. In addition to its acidic character, hydriodic acid possesses another property, which is not found in hydrochloric and hydrobromic acids. Since it splits up readily into hydrogen and iodine, it can act as a strong reducing-agent, especially at high temperatures. It has already been remarked that the aqueous solution of the gas turns brown, iodine being set free by the oxidizing action of the air; this change is greatly aided by the influence of light. At a high temperature hydrogen iodide is decomposed into H_2 and I_2, as is shown by the appearance of the violet iodine vapor. In organic chemistry, particularly, frequent use is made of the reducing power of this acid.

Formula of Hydriodic Acid.—The vapor density of this substance has been found to be 62.94. Its molecular weight is therefore 125.88. The atomic weight of iodine being 125.91 $(H = 1)$, it is seen that the molecular weight corresponds very closely to the formula $HI = 126.91$, and no other formula is possible.

DISSOCIATION.

49. When hydrogen iodide is subjected to a slow increase of temperature, it commences to decompose at a definite temperature slightly above 180° into hydrogen and iodine vapor. As the heating continues, the decomposition grows gradually greater till a point is finally reached when the gas mixture contains only the individual elements. If the mixture is then slowly cooled, the same stages are passed through in inverse order, so that the degree of decomposition at any one temperature is found to be the same, no matter whether the temperature was approached from above or below, it being only necessary that the particular temperature should be maintained for a sufficient length of time in both cases.

The phenomenon just described is to be observed with a great many substances. It is called **dissociation,** and was first studied in 1857 by H. SAINTE-CLAIRE DEVILLE.

The degree of decomposition of hydrogen iodide is, as we have seen, always the same for a definite temperature. It necessarily follows from this that if one starts with the uncombined elements, hydrogen and iodine, and heats them together long enough at a certain temperature, a gas mixture of exactly the same composition will be formed as that resulting from the decomposition of the hydrogen iodide at the same temperature. This is confirmed by experiment; e.g. equivalent amounts of iodine and hydrogen were heated in a sealed vessel by exposing it to the vapor of boiling sulphur (445°). The amount of hydrogen iodide finally produced was 79.0%, i.e. 21.0% of the gas mixture remained uncombined. Again, when a like vessel filled with hydrogen iodide was heated to the same temperature, it was found that 21.5% had decomposed —a figure very close to that obtained in the preceding experiment.

Such reactions, which lead to the same result, no matter whether we start with the one set of substances (H_2+I_2) or with the other ($2HI$), are called **reversible reactions.** When the final stage is reached, the sets, or "systems," are said to be in *equilibrium* with each other.

If we have a system of substances $A+B+\ldots$, which is partially changed into another system $P+Q+\ldots$, the equilibrium between the two systems is expressed by the sign $\rightleftarrows$; thus:

$$A+B\ldots\rightleftarrows P+Q\ldots$$

We saw that, in the preparation of hydrogen iodide, platinum black is used because it accelerates the combination. Neither this nor any other catalyzer, however, changes the proportional extent to which combination takes place. For instance, experiments have shown that at 350° 18.6% of the hydriodic acid is decomposed when no platinum-black is present, and that in the presence of this catalyzer the decomposition reaches 19%; these two figures are alike within the limits of experimental error. There is a theoretical reason why this must be so. If the catalyzer influenced the equilibrium, we could realize combination and decomposition by alternately adding and removing the catalyzer. Under constant conditions of temperature the system would absorb energy in one instance and evolve it in the other. The energy obtained in the latter case could be used to do work. Work would thus be gained from a system remaining at constant temperature, but according to the principles of thermodynamics this is impossible, since the production of work is always accompanied by a fall of temperature.

The question now arises, how such an equilibrium comes about, and why the decomposition of a compound that begins at a certain temperature does not complete itself. To this the kinetic theory of gases furnishes a satisfactory answer. According to this theory the molecules of gases are constantly in motion. While a constant *mean* velocity of the molecules may be assumed to exist for every temperature, the velocities of the *individual* molecules must be considerably different, because of their very frequent collisions with each other. The atoms of a molecule must also be supposed to be capable of changing their respective positions, for the repeated collisions of the molecules displace the atoms from their positions of equilibrium. These movements of the atoms are the more violent the greater the velocity of the molecules. It is easy to conceive that they may at last become so violent as to throw the atoms out of their sphere of mutual attraction. The molecule is thus broken up. In a body of gas at a definite temperature this will, however, only occur in those molecules whose velocity is above certain limits; hence we see a reason for *partial decomposition*. The explanation of *partial combination* is exactly analogous. The atoms set free from the molecules of the elements enter into the spheres of mutual attraction, and if their velocities are not great enough to resist the attraction, the different atoms unite.

In the case of the formation and decomposition of hydrogen iodide this can be conceived as follows: Two HI molecules meet in such a state of atomic movement that the H atoms enter the spheres of attraction of each other, and the I atoms likewise, so that H_2 and I_2 are formed. On the other hand, these molecules H_2 and I_2 may again meet in such a way that each H atom enters the sphere of attraction of one of the I atoms, whereupon two HI molecules are formed.

According to the above the state of equilibrium is to be accounted for by supposing that in the unit of time just as much passes from the one system into the other as *vice versa*. Until the state of equilibrium is reached, the amounts which pass from one system into the other in the unit of time are unlike.

In order to define more clearly this condition of equilibrium we must introduce the concept of **reaction velocity.** By this term we understand the number of moles transformed from one system into the other in the unit of time. Suppose that in the unit of volume (one liter, for instance) there are a moles of a substance A, which can undergo a chemical change into a substance B. If in the unit of time (say one minute) $\frac{a}{n}$ moles of A are converted into B, the reaction velocity S will be expressed by $\frac{a}{n}$. In case there are originally only $\frac{1}{2}a$ moles of A per liter, experiments have shown that the number of moles converted per minute is $\frac{1}{2}\frac{a}{n}$. We thus perceive that the *reaction velocity is proportional* to the number of gram-molecules per liter, or, in other words, *to the concentration.* This is a principle of very wide application; it is ordinarily called the **law of chemical mass action.** It finds a general expression in the equation

$$S=K\cdot a,$$

in which K is a constant factor, the **reaction constant,** or **velocity constant.**

50. Let us assume that the molecules of a compound are dissociated by heat into two others, the process being expressed by

$$A=B+C,$$

in which A, B and C represent single molecules. Of the substance A, a gram-molecules were originally present, but in the course of a definite time, t, x gram-molecules have undergone the above decomposition. The problem is to express the reaction velocity at any moment. At the beginning (during the first minute) the reaction velocity is proportional to a; after the time t, when the concentration has fallen to $a-x$, the amount converted during the succeeding minute will be proportional to $a-x$. The reaction velocity thus constantly diminishes. This being the case, it is evident that $s=k\cdot a$ and $s'=k(a-x)$ are not the true expressions, respectively, for the reaction velocity in the first minute and in the minute following the time t. They would be correct, if the concentration remained constant during these minutes instead of diminishing, as it does in reality. However, we can approach the real velocity by considering not one minute but a very small fraction of this unit of time, which we will call Δt; the smaller Δt is taken the less is the concentration change. Supposing that the quantity of A which is transformed in this very short period Δt is Δx, the expression $\frac{\Delta x}{\Delta t}$ must be very close to the real velocity, because it indicates the quantity transformed in a unit of time so small that the concentration scarcely diminishes during it. We approach the true velocity nearer and nearer according as we take Δt smaller and smaller, and when it is made infinitely small $\frac{\Delta x}{\Delta t}$ becomes the exact expression of the velocity. It is customary to express such infinitely small quantities by the letter d, thus: $\frac{dx}{dt}$. The mathematical expression for the velocity at a time t, when the concentration is $a-x$, thus becomes

$$S=\frac{dx}{dt}=K(a-x),$$

K being the velocity constant.

The above reaction is termed **unimolecular**. When two (like or different) molecules react with each other, the reaction is called **bimolecular**; it may be represented by the equation

$$A+B=C \quad \text{or} \quad =C+D+\ldots$$

The equation for the reaction velocity is different in this latter case. Assuming that originally a gram-molecules of A and b gram-molecules of B take part in the reaction, and that x gram-molecules of A and of B are decomposed at the end of the period t, there must be, respectively, $a-x$ and $b-x$ of the two substances present at this moment. The reaction velocity will then be proportional to the product of these quantities, thus:

$$S_1=\frac{dx}{dt}=K'(a-x)(b-x),$$

in which K' is again a constant; for suppose that there were only one molecule of A present; the possibility of its reacting with a molecule of B would then be proportional to the number of molecules of B. When there are $a-x$ molecules of A this possibility becomes $a-x$ times as large.

It is assumed in the above that the temperature is constant. We shall see in § 104 that this factor has a great influence on the reaction velocity.

51. The manner of expressing the condition of equilibrium is now plain. Assuming that the reaction velocity of the one system is S and that of the other S', equilibrium must exist when

$$S=S'.$$

The *state of equilibrium* may therefore be defined as *that state in which the reaction velocities of both systems have become equal.*

Let us apply these considerations to the dissociation of hydrogen iodide. This may be expressed by

$$2HI \rightleftarrows H_2+I_2.$$

If a gram-molecules HI per unit volume are present originally and x of these are decomposed after a given period, the reaction velocity at this moment (since in this case $a=b$, and the reaction is evidently bimolecular) is

$$S=C(a-x)^2,$$

C being a constant.

From the x gram-molecules of hydrogen iodide $\frac{x}{2}$ gram-molecules of hydrogen and an equal amount of iodine have been formed. The velocity of formation of HI from H_2 and I_2 is therefore expressed by the equation

$$S'=C'\left(\frac{x}{2}\right)^2,$$

in which C' is a constant. Accordingly equilibrium will exist when

$$C(a-x)^2=C'\left(\frac{x}{2}\right)^2, \text{ or } \left(\frac{x}{a-x}\right)^2=K,$$

in which K is substituted for $\frac{4C}{C'}$.

This equation may be written in a slightly different way, since in gases the number of molecules per unit volume is proportional to the pressure (§ 31). Assuming that at a given moment the pressure of the hydrogen iodide still present is p, that of the hydrogen is p_1, and that of the iodine vapor p_2, the equilibrium constant, K, can be represented by the expression

$$\frac{p_1p_2}{p^2}=K.$$

It has been ascertained that the dissociation is less if the hydrogen iodide was originally mixed with hydrogen or with iodine vapor. The necessity of this being true follows immediately from the above equation, for the addition of these gases amounts to an increase of p_1 or p_2. If K is to remain constant, p, or in other words the mass of undissociated hydrogen iodide, must increase. We see also from the equation that the same increase of H_2 or of I_2 must have the same influence on the equilibrium. A further conclusion from this equation is that, when p, p_1 and p_2 are increased n-fold, i.e. when hydrogen iodide undergoing dissociation is compressed or expanded at a constant temperature, the degree of dissociation must remain unaltered, since

$$\frac{np_1\cdot np_2}{(np)^2}=\frac{p_1p_2}{p^2}.$$

This, too, is confirmed by experiment.

In the dissociation of hydrogen iodide the gas volume does not change, since two molecules (2HI) yield two molecules (H_2 and I_2). In all such cases the degree of dissociation must be independent of the volume, because an increase or decrease in the latter causes changes in the concentration of the reacting gases which are proportional to each other, and hence the factor representing the concentration falls out of the equation.

Hydrogen iodide is also decomposed by light. It is a peculiar fact that this dissociation is unimolecular ($HI=H+I$), while that caused by rise of temperature is bimolecular. This may be demonstrated by the following very general method. When the reaction is unimolecular, the equation for the velocity of decomposition is $\frac{dx}{dt}=K(a-x)$. When, however, it is bimolecular ($2HI = H_2 + I_2$), the equation becomes $\frac{dx}{dt} = K(a-x)^2$. With the help of integral calculus these equations can be solved for K; from the first we find

$$K = \frac{1}{t} \log_e \frac{a}{a-x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\log_e$ is the natural logarithm, and from the second:

$$K = \frac{1}{t} \frac{x}{a(a-x)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If now we determine x for various values of t, the values of K can be calculated; they must be constant. If this constancy appears in (1), the reaction is unimolecular, if in (2), bimolecular.

FLUORINE.

52. This element was first isolated from its compounds by MOISSAN in 1886. It occurs in nature chiefly in combination with calcium as *fluor spar*, CaF_2, and in certain rare minerals.

The great difficulty in obtaining it in the free state is due to its very great affinity, which makes it unite with other elements even at ordinary temperatures. As yet it has only been successfully prepared by the electrolysis of pure anhydrous hydrofluoric acid in which potassium fluoride has been dissolved to make the liquid a conductor.

The manner in which MOISSAN accomplished this is interesting. A mixture of about 200 g. anhydrous hydrofluoric acid and 60 g. hydrogen potassium fluoride is introduced into a copper U-tube (Fig. 23) of a capacity of about 300 c.c., which has two lateral exit-tubes. The open ends of the U-tube are closed with stoppers FF, made of fluor spar and wrapped in very thin sheet platinum.

The cylindrical electrodes tt of platinum-iridium pass through the stoppers and are held in place by the copper screws EE, which fit tightly to the ends of the U-tube, with the help of a band of lead P.

During the electrolysis the apparatus is kept at the constant temperature of −23° (by boiling methyl chloride). The free fluorine, which is given off as a gas at the positive electrode, is first passed through a platinum vessel that is cooled by a mixture of solid carbon dioxide and alcohol, in order to condense the acid fumes which were carried over with it. The last traces of the acid are removed by conducting the gas through two platinum tubes containing sodium fluoride, which absorbs the hydrofluoric acid. The free fluorine gas was collected by MOISSAN in a platinum tube, whose two ends were closed with plates of fluor spar so that one could look through.

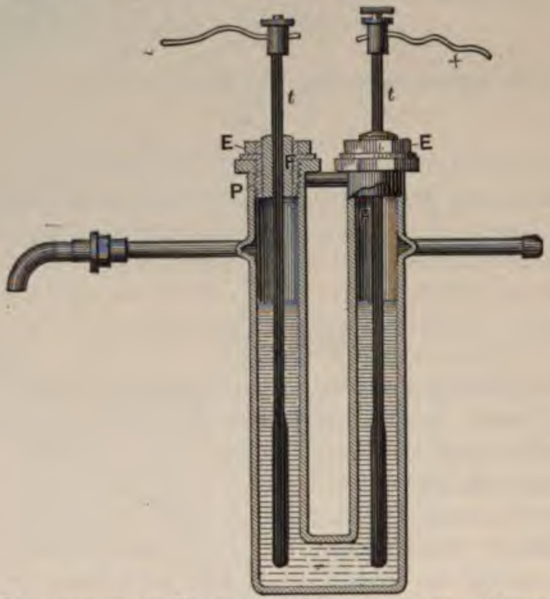


FIG. 23.—PREPARATION OF FLUORINE BY ELECTROLYSIS. (AFTER MOISSAN.)

Later MOISSAN found that perfectly pure fluorine attacks glass but very slowly, so that the gas may be collected in glass vessels.

Physical Properties.—Fluorine is a gas with a very pungent odor and a greenish-yellow color, which is somewhat paler than that of chlorine. As a liquid it boils at $-187°$ and is bright yellow. It can be condensed in a glass vessel. When cooled by liquid hydrogen it freezes to a white mass, that melts at $-223°$. The specific gravity of the gas is 19 ($O=16$), that of the liquid 1.14 (water$=1$).

Chemical Properties.—Of all the elements now known fluorine has the strongest tendency to form compounds. It combines with hydrogen in the dark at ordinary temperatures in an explosive manner. MOISSAN demonstrated this with the help of the above apparatus by reversing the electric current while fluorine was being generated; thus a mixture of hydrogen and fluorine was formed, which at once exploded. As low as $-252.5°$, solid fluorine unites with liquid hydrogen immediately, producing a flame. Finely divided carbon ignites instantaneously in fluorine gas, forming CF_4. With sulphur, red phosphorus, lime and other substances fluorine reacts vigorously even at $-187°$. Fluorine combines with most metals instantly and violently; it does not unite with oxygen, even when it is heated with the latter to 500° or mixed in the liquid state with liquid oxygen at $-190°$. The alkali metals (potassium and sodium) and the alkaline-earth metals (calcium, strontium, barium) take fire in fluorine gas at ordinary temperatures with the formation of fluorides. Finely divided iron glows faintly in it. Copper becomes covered with a layer of copper fluoride, CuF_2, which protects it against farther corrosion; hence the possibility of employing this metal for fluorine generators. Gold and platinum are not attacked by fluorine,—a rather striking fact, since these metals are acted on by chlorine, which otherwise displays a weaker chemical affinity.

Fluorine reacts readily with hydrogen compounds; e.g. water is decomposed by it at ordinary temperatures into hydrofluoric acid and strongly ozonized (as high as 14% by volume) oxygen. It sets chlorine free from potassium chloride, forming potassium fluoride.

The *molecule* of gaseous fluorine is expressed by the formula F_2. Its vapor density being 19, the molecular weight is 38. Inasmuch as no fluorine compound contains less than 19 g. fluorine per gram-molecule, but frequently a multiple of this amount, the atomic weight of fluorine becomes 19 and its molecular formula F_2.

HYDROGEN FLUORIDE, or HYDROFLUORIC ACID, HF.

53. This compound was discovered by SCHEELE in 1771 upon heating together fluor spar and sulphuric acid:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

This is still the usual method of preparing the substance. A mixture of powdered fluor spar and dilute sulphuric acid is distilled in an apparatus of platinum or lead, since glass is instantly attacked by hydrofluoric acid. The distillate is an aqueous solution of the acid, which for the above reason must be preserved in bottles of lead or caoutchouc.

By direct synthesis from its elements (§ 52) hydrofluoric acid may also be obtained. Another method is by the action of hydrogen on a fluorine compound; e.g. silver fluoride, when heated in a current of hydrogen, gives hydrogen fluoride.

Still other methods are by the action of fluorine on hydrogen compounds (§ 52) and by the direct decomposition of certain compounds, such as hydrogen potassium fluoride, KF·HF, which splits up on heating into the two fluorides. This last reaction is made use of when anhydrous acid is sought.

Physical Properties.—Anhydrous hydrofluoric acid is a colorless liquid at ordinary temperatures. It boils at 19.5° and solidifies at $-102.5°$. Sp. g. $(H=1)=0.9879$ at 15°. It has an extremely pungent odor and is very poisonous when inhaled. It is very soluble in water.

Chemical Properties. — The aqueous solution of hydrogen fluoride, the "hydrofluoric acid" of commerce, possesses entirely the character of an acid; it evolves hydrogen with most metals, the precious metals, however, and also lead, being unaffected by it. The fluorides of the metals are, in general, soluble in water; some, however, such as those of copper and lead, dissolve with difficulty, while those of the alkaline earths (Ca, Sr and Ba) are insoluble. It is a peculiar characteristic of the alkali fluorides that they are able to combine with a molecule of the acid, forming double fluorides like that described above, KF·HF.

This characteristic is probably due to the fact that in aqueous solution the molecule of hydrofluoric acid is H_2F_2. The formation of such double molecules is often observed for acids (especially organic acids). It is called *association*. Thus liquid water consists in all probability of H_4O_2 molecules.

The most important property of the gas for practical purposes is that it attacks glass (*cf.* § 193). As a result it finds extensive use in etching glass.

Glass may be etched in two ways—with a solution of the gas or with the gas itself. In the first case the etching is shiny and transparent; in the second dull. The glass object is covered with a coat of wax in which the figures or letters which one desires etched on the glass may be drawn with a stylus. Then the object is either dipped in dilute hydrofluoric acid for a while or set over a leaden dish which contains a mixture of sulphuric acid and calcium fluoride kept slightly warm by a low flame. Only the places where the coating was removed are attacked, so that, when the latter is subsequently dissolved off (by turpentine or alcohol), the etch-figure is visible.

Moissan has proved that glass is also attacked by perfectly dry hydrofluoric acid gas.

The *formula of hydrofluoric acid gas* is HF, which can be determined in exactly the same way as was done for the analogous chlorine and bromine compounds.

Compounds of the Halogens with each other.

54 The halogens, or salt-formers, i.e. the elements fluorine, chlorine, bromine and iodine (so-called because they form salts with metals by direct combination), can unite with each other to form rather unstable compounds. In general the most stable of these compounds are those whose component halogens show the greatest dissimilarity.

Iodine unites with fluorine to form a compound IF_5, which can exist even in the gaseous state. There is also a BrF_3; chlorine and fluorine, however, do not combine with each other.

Chlorine and bromine at low temperatures give an unbroken series of mixed crystals (§ 212, 2), but form no compound. With iodine chlorine gives two compounds, ICl and ICl_3. It depends on the quantity of chlorine present as to whether the former or the latter is obtained. ICl is a reddish brown oil that eventually yields crystals melting at 24.7°; it boils at 101.3°. Water decomposes it into iodic acid, iodine and hydrogen chloride. It exists in two modifications. ICl_3 crystallizes in long yellow needles and on fusing dissociates almost completely into ICl and Cl_2. In a small quantity of water it dissolves almost unchanged; but a larger quantity of water decomposes it partially into hydrogen chloride and iodic acid.

Bromine and iodine give only one compound, BrI, which is considerably dissociated in the liquid as well as in the gaseous state.

Oxygen Compounds of the Halogens.

With the exception of fluorine, the halogens are known to form various oxygen compounds, having the common property of instability, i.e. of being easily decomposed. Most of them can combine with water, forming acids. Oxides which show this latter property are called **acid anhydrides.** The acids which are thus formed from the halogen oxides contain each but one hydrogen atom, and this can be replaced by a metal. Acids containing one hydrogen atom which can be thus substituted are called **monobasic.**

HYPOCHLOROUS OXIDE. CHLORINE MONOXIDE, Cl_2O.

55. This compound can be prepared by passing chlorine over dry mercuric oxide at a low temperature:

$$2HgO + 2Cl_2 = Cl_2O + HgO \cdot HgCl_2.$$

Hypochlorous oxide is a brownish-yellow gas at ordinary temperatures. It can be condensed by strong cooling to a dark-brown liquid, which boils at +5°. It is an extremely dangerous substance, especially in the liquid state, since the slightest mechanical disturbances make it explode vigorously, breaking up into its elements. It is possible to distil it without decomposition, only when everything with which it comes in contact is entirely free from dust (organic matter). It acts upon sulphur, phosphorus and compounds of carbon with explosive violence.

The *composition* of this compound was determined by BALARD in the following way: He introduced 50 vols. of the gas into a tube over mercury and decomposed it by gently warming. He thus obtained a mixture of chlorine and oxygen which occupied somewhat less than 75 vols. After the chlorine was removed by caustic potash, 25 vols. remained, i.e. 50 vols. chlorine were present, the slight difference which was observed being ascribable to the fact that a little chlorine had united with the mercury in the tube. 1 vol. hypochlorous oxide yielded therefore 1 vol. chlorine and ½ vol. oxygen. This indicates the formula Cl_2O:

$$\underset{\text{2 vols.}}{2Cl_2O} = \underset{\text{2 vols.}}{2Cl_2} + \underset{\text{1 vol.}}{O_2}.$$

The vapor density of the compound was found to be 3.03 (air = 1), or 43.63 (O = 16). Its molecular weight therefore becomes 87.26, corresponding to the formula Cl_2O (2Cl = 71; O = 16; sum = 87).

HYPOCHLOROUS ACID, HClO.

56. When chlorine monoxide, Cl_2O, is passed into water, it is absorbed; the solution contains hypochlorous acid:

$$Cl_2O + H_2O = 2HClO.$$

This compound is known only in aqueous solution. Its composition is studied in its salts.

The same aqueous solution can also be obtained by adding finely powdered mercuric oxide to chlorine water. Distillation may be employed to purify the solution of the acid. Another method is to add at once enough mercuric oxide to form the oxychloride, $HgO \cdot HgCl_2$, which is insoluble in water and can be removed from the hypochlorous acid solution by filtration:

$$HgO + 2Cl_2 + H_2O = \underset{\text{Soluble.}}{HgCl_2} + 2ClOH.$$

$$2HgO + 2Cl_2 + H_2O = \underset{\text{Insoluble.}}{HgO \cdot HgCl_2} + 2ClOH.$$

Still another method of preparing the acid solution is to lead chlorine into the solution of a base, e.g. potassium hydroxide, at the ordinary temperature, whereupon a salt of hypochlorous acid (hypochlorite) is formed:

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

By carefully treating the hypochlorite with the equivalent amount of nitric acid the hypochlorous acid is set free and can be separated from the salts by distillation.

When concentrated, the aqueous solution of hypochlorous acid has a golden color. It is unstable; only dilute solutions can be distilled without decomposition. It oxidizes vigorously, breaking up into oxygen and hydrochloric acid:

$$2ClOH = 2HCl + O_2.$$

On the addition of hydrochloric acid all the chlorine of both compounds is set free:

$$HClO + HCl = Cl_2 + H_2O.$$

The hypochlorites act just like the free acid, since the presence of very weak acids, e.g. the carbonic acid of the air, serves to liberate hypochlorous acid. They are therefore extensively employed as bleaching agents (§ 27). A solution of sodium hypochlorite (*eau de Javelle*) is used for this purpose, but chloride of lime ("bleaching powder," § 258) deserves particular notice. The latter is obtained by treating lime with chlorine at ordinary temperatures. The bleaching action of hypochlorous acid is twice as great as that of the chlorine which it contains would be, if the latter were to act in the free state:

$$2Cl + H_2O = 2HCl + O \quad \text{and} \quad 2ClOH = 2HCl + 2O.$$

However, it should be remembered that *two* atoms of chlorine were necessary to form the *one* HClO molecule:

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

On shaking an aqueous solution of hypochlorous acid with mercury a brownish-yellow precipitate of mercuric oxychloride, $n\text{HgO}\cdot\text{HgCl}_2$, is formed, which is insoluble in hydrochloric acid. Chlorine water, on the other hand, when shaken with mercury, gives white mercuric chloride, $HgCl_2$ (sublimate). These reactions enable us to distinguish between the two substances.

In a dilute aqueous solution of chlorine we have the following equilibrium:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO,$$

as is shown by the facts that the solution reacts distinctly acid toward litmus and that the hypochlorous acid can be separated from the hydrochloric acid by distillation.

The difference in the action of chlorine water and a solution of hypochlorous acid on mercury is due to the fact that in the above equilibrium the system $Cl_2 + H_2O$ is by far the predominant one.

CHLORINE DIOXIDE, ClO_2.

57. This gas is formed when potassium chlorate, $KClO_3$, is treated with concentrated sulphuric acid. Chloric acid is at first set free and this decomposes as follows:

$$\underset{\text{Chloric acid.}}{3HClO_3} = \underset{\text{Perchloric acid.}}{HClO_4} + 2ClO_2 + H_2O.$$

Chlorine dioxide is a dark-yellow gas. It can be condensed to a liquid, which boils at 9.9° and solidifies at $-79°$ to a yellow crystalline mass. It has a peculiar odor resembling chlorine and burned sugar.

Chlorine dioxide is extremely explosive; warming, jarring or contact with organic substances causes it to explode with violence. Light slowly decomposes it.

The following experiments give one an idea of the vigor with which it causes oxidation. (1) When finely powdered sugar is mixed carefully with potassium chlorate and a drop of concentrated sulphuric acid is added, the whole mass bursts into flame. The chlorine dioxide set free makes the sugar burn at ordinary temperature. (2) Place a few pieces of yellow phosphorus and some crystals of potassium chlorate under water and allow a few drops of concentrated sulphuric acid to flow down on the two substances. The phosphorus at once burns under water with a brilliant light.

Chlorine dioxide is soluble in water. Such a solution can be easily prepared by floating a little porcelain cup in a large crystallizing-dish with a flat brim and containing 220 c.c. water, putting into the cup 12 g. potassium chlorate and adding a cooled mixture of 44 c.c. concentrated sulphuric acid and 11 c.c. water. The crystallizing-dish is then covered with a glass plate. The chlorine dioxide evolved dissolves in the water, forming a yellow solution.

When a base is added to a chlorine dioxide solution, a chlorite (§ 58) and a chlorate are formed:

$$2KOH + 2ClO_2 = \underset{\text{Pot. chlorite.}}{KClO_2} + \underset{\text{Pot. chlorate.}}{KClO_3} + H_2O.$$

This reaction proceeds very slowly in dilute solution.

The *composition* of chlorine dioxide was determined by Gay-Lussac as follows: He allowed the gas to flow through a capillary tube with three bulbs. By heating the part of the tube in front of the bulbs he decomposed the gas, the action being non-explosive in so narrow a space. Thus there was obtained in the bulbs a mixture of oxygen and chlorine in the same proportions as they are contained in the compound. The chlorine was absorbed by potash and the residual gas (oxygen) was passed over into a measuring-tube. The capacity of the bulbs being known, it was possible from these data to calculate the volume ratio of oxygen and chlorine. It was found that 100 vols. of the oxide yields 67.1 vols. oxygen and 32.9 vols. chlorine. This ratio is very close to that of 1: 2, represented by the formula ClO_2:

$$\underset{\text{2 vols.}}{2ClO_2} = \underset{\text{1 vol.}}{Cl_2} + \underset{\text{2 vols.}}{2O_2}.$$

This formula is also confirmed by the vapor density, which was found to be 34.5 at 10.5°, while the formula ClO_2 demands $\frac{35.5+2\times16}{2}=33.7$.

CHLOROUS ACID, $HClO_2$.

58. This acid is unknown in the pure state. Its sodium salt is formed by the action of sodium peroxide solution on a chlorine dioxide solution:

$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2.$$

The silver salt, $AgClO_2$, is a yellow crystalline powder, as is also the lead salt, $Pb(ClO_2)_2$; they are both difficultly soluble in water, and break up even on warming to 100° in an explosive manner. The anhydride of chlorous acid, corresponding to the formula Cl_2O_3, is not known.

CHLORIC ACID, $HClO_3$.

59. The chlorates of potassium or barium are the usual starting-points for the preparation of chloric acid. When dilute sulphuric acid is added to the solution of the barium chlorate, barium sulphate is precipitated and a dilute solution of chloric acid is obtained, which may be filtered off from the sulphate and dried in a vacuum desiccator over concentrated sulphuric acid. In this way a 40% solution of the acid may be obtained. On concentrating it any farther, decomposition takes place, oxygen being evolved and perchloric acid formed. The concentrated acid is a powerful oxidizing agent; wood or paper ignites when brought in contact with it. It oxidizes hydrochloric acid, chlorine being given off; further sulphuretted hydrogen, sulphurous acid and others, even in dilute solution. The following reaction is very characteristic of chloric acid. When indigo solution is added to a dilute solution of the acid, the former is not decolorized; however, on the addition of a little sulphurous acid the color disappears, since the chloric acid is thereby reduced to lower oxides.

The *salts* are all soluble in water, that of potassium being somewhat difficultly so, however.

The *composition of chloric acid* was ascertained by STAS from an analysis of silver chlorate. An accurately weighed amount of the latter was reduced by a solution of sulphurous acid to silver chloride and this was filtered off and weighed. Since he knew from previous investigations the exact composition of silver chloride, the analysis of the silver chlorate was complete. STAS found thus that silver chlorate consists of

Silver	56.3948%
Chlorine	18.5257%
Oxygen	25.0795%
Total	100.0000%

The atomic weight of silver is 107.93; that of chlorine 35.45; that of oxygen 16.00. We then find that the ratio of the atoms in this salt is

$$\frac{56.3948}{107.93}=0.52;\quad \frac{18.5257}{35.45}=0.52;\quad \frac{25.0795}{16.00}=1.58;$$

i.e. very close to 1:1:3, from which it follows that the empirical formula of the salt is $AgClO_3$, that of the acid itself $HClO_3$.

PERCHLORIC ACID, $HClO_4$.

60. This compound is obtained by distilling potassium perchlorate with an excess of sulphuric acid of 96–97.5% *in vacuo:*

$$KClO_4+H_2SO_4=KHSO_4+HClO_4.$$

Pure perchloric acid boils at 39° under a pressure of 56 mm. Hg, and has a specific gravity of $D_4^{22}=1.764$ at 22°. It is a colorless liquid which does not solidify on being cooled with solid carbon dioxide and alcohol (about −80°). It decomposes slowly, taking on a dark color. With water it forms different hydrates; the best known of them is the monohydrate, $HClO_4 \cdot H_2O$, which melts at 50°; with more water a thick oily liquid is formed, similar to concentrated sulphuric acid. Such an acid contains 71.6% $HClO_4$; it distils without change in composition at 203° and has a specific gravity of 1.82. The dilute solution of the perchloric acid is stable.

In the concentrated state perchloric acid is a very strong oxidizing agent. When a little is dropped on wood or paper, these ignite with explosion. Very painful flesh-wounds are produced by it. When dilute, it does not, however, release its oxygen nearly so readily as chloric acid. It can, for example, be gently warmed with hydrochloric acid without giving off chlorine, and it is not reduced by sulphurous acid. By these facts and by its yielding no chlorine dioxide with sulphuric acid it may be distinguished from chloric acid.

The salts of perchloric acid, perchlorates, are all soluble in water; that of potassium and especially that of rubidium are, however, very difficultly soluble in cold water.

The *composition* of perchloric acid has been determined, as in the case of chloric acid, by the analysis of a salt, in this instance the potassium salt. A weighed amount of the latter is heated to drive off all the oxygen. The loss in weight indicates the amount of the latter. The analysis of the remaining potassium chloride, KCl, shows the amounts of potassium and chlorine. From these data it is found, in the same manner as with chloric acid, that the empirical formula of the salt is $KClO_4$, that of the acid, therefore, $HClO_4$.

Chlorine heptoxide, Cl_2O_7, is the oxide corresponding to perchloric acid:

$$2HClO_4 - H_2O = Cl_2O_7.$$

It may be obtained by slowly adding perchloric acid to phosphorus pentoxide cooled below − 10°. By distillation on a water bath the oxide is obtained as a colorless liquid, which boils at 82°. It is more stable than the other oxides of chlorine; it neither attacks paper nor acts on sulphur or phosphorus in the cold.

OXYGEN COMPOUNDS OF BROMINE.

61. Although no compounds with oxygen alone are known, there are two oxygen acids, viz., hypobromous and bromic.

Hypobromous acid, HBrO, can be obtained in the same way as HClO, namely, by shaking up bromine water and mercuric oxide together. The dilute solution can be distilled *in vacuo*, and has properties entirely analogous to those of hypochlorous acid.

Bromic acid, $HBrO_3$, can be obtained from the barium salt with sulphuric acid or from the silver salt with bromine-water:

$$5AgBrO_3 + 3Br_2 + 3H_2O = \underset{\text{Insol.}}{5AgBr} + 6HBrO_3.$$

It is also formed when chlorine is passed into bromine-water:

$$Br_2 + 5Cl_2 + 6H_2O = 2HBrO_3 + 10HCl.$$

It corresponds in its behavior with chloric acid. Many reducing-agents, such as hydrogen sulphide and sulphurous acid, are able to extract all its oxygen. Most of its salts are difficultly soluble in water. When heated, they give up all their oxygen.

OXYGEN COMPOUNDS OF IODINE.

62. When iodine is introduced into a cold dilute solution of caustic potash or soda, a colorless liquid is obtained, which has other properties when fresh than it has later. When freshly prepared it decolorizes indigo solution and iodine is liberated on the addition of very weak acids. Later on these two properties disappear. It is therefore to be supposed that a hypo-iodate KIO is first formed, and that this is changed slowly to KI and KIO_3. At the boiling-point the change takes place almost instantly.

Iodine pentoxide, I_2O_5, is the anhydride of iodic acid, since it can be obtained by heating this acid to 170°,

$$2HIO_3 = H_2O + I_2O_5,$$

and yields the same acid when dissolved in water. It is a white crystalline substance, which breaks up into its elements at 300°.

Iodic acid, HIO_3, is best prepared by the oxidation of iodine with nitric acid:

$$3I_2 + \underset{\text{Nitric acid.}}{10HNO_3} = 6HIO_3 + \underset{\text{Nitric oxide.}}{10NO} + 2H_2O.$$

Iodic acid is crystalline and easily soluble in water. It is a powerful oxidizing-agent, setting free chlorine from hydrochloric acid, for example.

$$2HIO_3 + 10HCl = I_2 + 5Cl_2 + 6H_2O.$$

It reacts instantaneously with hydriodic acid, all the iodine of both compounds being precipitated:

$$5HI + HIO_3 = 3H_2O + 6I.$$

The salts of this acid, the iodates, are in general not very soluble in water; however, those of the alkali metals dissolve rather easily.

Periodic acid, $HIO_4 + 2H_2O$, is formed by the action of iodine on perchloric acid:

$$HClO_4 + I + 2H_2O = HIO_4 \cdot 2H_2O + Cl.$$

It is a colorless crystalline solid that is entirely decomposed at 140° into iodine pentoxide, oxygen and water (§ 145).

NOMENCLATURE.

63. The system of naming the various halogen **oxygen-acids** is a general one, which is also used for the acids of other elements. The best-known acid usually has the suffix *-ic*, e.g. chloric acid, phosphoric acid, sulphuric acid, etc. Acids that contain more oxygen have in addition the prefix *per-*, thus perchloric acid and persulphuric acid. Acids containing less oxygen have the suffix *-ous*, e.g. chlorous acid, sulphurous acid, phosphorous acid, etc. Those which contain still less oxygen have the suffix *-ous* and also the prefix *hypo-*, e.g. hypochlorous acid, hyposulphurous acid and hypophosphorous acid.

The names in use in pharmaceutical chemistry (see the National Pharmacopœia) follow the Latin. Thus we have *Acidum sulphuricum* (sulphuric acid) and *Acidum sulphurosum* (sulphurous acid).

The names of the **salts** of the best-known (*-ic*) acids end in *-ate*, e.g. potassium chlorate, -sulphate, -phosphate. The salts of the *-ous* acids have the ending *-ite*, as potassium chlorite, -sulphite, -phosphite. The salts of *hypo- -ous* acids are called *hypo- -ites;* thus sodium hypochlorite, -hyposulphite, -hypophosphite.

The names of the anhydrides correspond to those of their acids.

In naming **oxides** the name of the element with or without the ending *-ic* is used, unless there is more than one oxide. Where there are two oxides, the name of the one with the more oxygen ends in *-ic*, that of the other in *-ous*, e.g. mercuric oxide, arsenic oxide, mercurous oxide, arsenious oxide. An oxide with less oxygen than the *-ous* compound is given the prefix *hypo-*, and one with more than the *-ic* oxide the prefix *per-*, as in the case of acids, thus hypochlorous oxide, lead peroxide. In some cases, for the sake of euphony, the suffix is added to the Latin instead of the English stem, as cuprous, ferric, etc.

For historical reasons many names now in use do not conform to this system. In some instances the oxide first discovered took the suffix *-ic*, and those subsequently discovered were named accordingly, as in the case of the nitrogen oxides (§ 119).

It is not uncommon to speak of oxides of the general formula M_2O_3 as *sesquioxides*.

A much more rational system is to indicate the number of atoms of oxygen by the Latin or Greek numeral, e.g. chlorine protoxide, or monoxide, iodine pentoxide, etc.

SUMMARY OF THE HALOGEN GROUP.

64. It is evident from the foregoing descriptions that the properties of the halogens and their compounds possess great similarity among themselves. A closer study reveals the fact that the increase of atomic weight is accompanied by a gradual change of physical and chemical properties. For example, let us notice the physical properties:

	F.	Cl.	Br.	I.
Atomic weight.........	19	35.45	79.96	126.97
Melting-point..........	−223°	−102	− 7	+113
Boiling-point...........	−187°	− 33	+63	+200
Sp. g. (liquid or solid)...	1.14(liquid)	1.33	3.18	4.97
Color................	pale greenish-yellow.	greenish-yellow	brown	violet-black

It is seen that the values of the physical constants increase on the whole with the atomic weight. The purely metalloid character of the first three is also found in iodine, although in the case of the latter an external characteristic of metals, viz., metallic lustre, is at once noticeable.

The affinity for hydrogen decreases as the atomic weight increases. We saw that fluorine combines with this element even in the dark and at very low temperatures in an explosive manner; iodine unites with hydrogen directly only at a high temperature and the compound is easily decomposed by heat. Inversely, the oxygen compounds are the more stable the higher the atomic weight of the halogen. While a halogen of low atomic weight displaces a halogen of higher atomic weight from its hydrogen compound, e.g.

$$HI + Cl = HCl + I,$$

the halogen with higher atomic weight can on the other hand replace one with lower in its oxygen compounds, setting that other one free:

$$KClO_3 + I = KIO_3 + Cl.$$

ELECTROLYTIC DISSOCIATION.

65. In § 30 it was stated that the properties of an aqueous solution of hydrogen chloride differ widely from those of the dry gas. It was also stated there that many other substances undergo a similar change of properties when they are dissolved in water. We may now consider the nature of this change.

If we investigate the freezing-point depression of the aqueous solution of an acid, base or salt of known concentration, we find that the depression does *not* correspond with that calculated from the accepted molecular weight (§ 43). The freezing-point depression and the boiling-point elevation are both greater than they should be. A 1% sodium chloride solution would, for example, be expected to show a depression of $\frac{19}{58.5}=0.325°$, the molecular depression for water (§ 43) being 19, i.e. $AM=19$, and the molecular weight of sodium chloride 58.5. In reality, however, the depression is found to be 1.9 times as great, namely, 0.617°. As the osmotic pressure is proportional to the freezing-point depression (§ 42), it must also be greater than the calculated amount.

The fact at once occurs to us that gases, to which dissolved substances have been found to show close analogy, also exhibit a similar phenomenon. In numerous instances the pressure exerted by a definite weight of gas occupying a definite volume at a definite temperature is greater than the calculation indicates.—This is but another phase of the observation that the vapor density of some gases is abnormally low at certain temperatures (§ 47).—This is explained by assuming a breaking up of the gas molecules; the number of particles free to move about is thus increased and accordingly the pressure becomes greater. This phenomenon is known as *dissociation* (§ 49).

In the case of abnormal osmotic pressure we are led to a similar explanation by assuming that the molecules are split up into several independent particles. A difficulty arises, however, when we try to conceive the nature of this division. In solutions of salts in water it would be possible to assume a hydrolytic separation, i.e. into free base and free acid (p. 104), which would necessarily be complete in dilute solutions of the salts of strong acids and bases, inasmuch as the osmotic pressure of such solutions in concentrations of $\frac{1}{10}$ normal (§ 93), for instance, amounts to double the calculated pressure. There are, however, serious objections to such a hypothesis. In the first place, it has never yet been possible to separate such a solution by diffusion into the free base and free acid which it is supposed to contain. A second and still more serious objection is that an acid or base in an aqueous solution by itself exerts an osmotic pressure greater than that calculated. Here, however, hydrolytic dissociation is impossible.

The question as to the real nature of the division has found its answer in a consideration of the relation which exists between the abnormal osmotic pressure and the transmission of the electric current. ARRHENIUS observed that only those substances which conduct the electric current in aqueous solution, namely, acids, bases and salts, show the above-mentioned abnormalities in osmotic pressure. When these substances are dissolved in another liquid than water, the resulting solution is a non-conductor, but at the same time its osmotic pressure again assumes the normal. These facts enable us to perceive the connection between the apparently disconnected phenomena of abnormal osmotic pressure and electrolytic conduction.

In order to understand this relation it is necessary to know the usual explanation of electrolytic conduction. Let us take hydrochloric acid as an example. Perfectly dry hydrochloric acid gas is a non-conductor, as is also perfectly pure water. However, when the gas is dissolved in water, a solution is obtained which transmits electricity very well. Evidently a certain reaction must have resulted from the mixing of the water and the hydrogen chloride. We were led to surmise this above (§ 29), when it was found that this gas solution does not obey HENRY's law. Since during the transmission of the current the hydrogen chloride is broken up into hydrogen and chlorine while the water remains unchanged, it must be assumed that the hydrogen chloride molecules are the ones which have undergone a change.

The phenomena of electrolytic conduction now find their complete explanation in the assumption that the change which the hydrochloric acid underwent consisted in a separation of its molecules into electrically charged atoms (*ions*) (§ 267). This separation may have been complete or partial, the extent depending upon the concentration among other things. When a current passes through the solution, the negatively charged chlorine ions (the *anions*) are drawn toward the positive electrode (anode); they become electrically neutral on contact with the latter and escape from the liquid. Similarly the positively charged hydrogen ions (*cations*) wander toward the negative electrode (cathode). In this way conduction goes on, the undivided molecules having no part in it. This division of the molecules is known as **electrolytic dissociation,** or **ionization.**

The *existence of free ions* in the solution of an electrolyte is demonstrated by OSTWALD in the following manner. The tube *abcd*, Fig. 24, is nearly filled with dilute sulphuric acid. The narrowed portion *bc* is about 40 cm. long. A rod of amalgamated zinc is lowered into *a* to serve as the positive electrode, while a platinum wire is fused into *d* at *p* for a negative electrode. If connection is made with a battery of ten accumulators, there is an *immediate* evolution of hydrogen at *p*. The passage of the current through the liquid results in the formation of zinc sulphate around the bar in *a*:

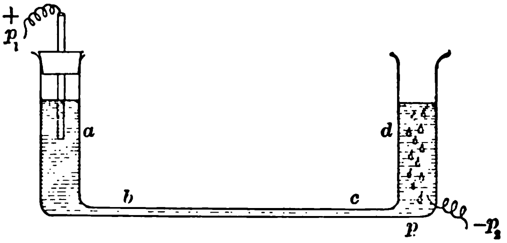


FIG. 24.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Now if this hydrogen has to pass through *bc* to *p*, it must cover the 40 cm. in a very brief space of time. However, it has been shown both by investigations which cannot be described here and by calculus that this migration would take many hours. The hydrogen appearing at *p* as soon as the circuit is closed cannot, therefore, come from *a*; the most natural explanation is to suppose that there are already free ions in the neighborhood of *p* and that they are discharged by the current and given off from the liquid as free hydrogen.

In order that this hypothesis of dissociation into ions may also account for abnormal osmotic pressure, it must be assumed that the ions are independent particles, just as free to move as the molecules are supposed to be. The number of freely moving particles in the same volume is thus increased. Hence, whether the amount of ionization is calculated from the electrical conductivity or from the osmotic pressure, the result should be the same according to the above hypothesis. This is found to be the case.

Supposing that every molecule yields n ions by the dissociation and that the dissociated portion of the whole number of molecules is γ, the number of freely moving particles is

$$1-\gamma+n\gamma=1+\gamma(n-1).$$

The osmotic pressure must therefore be $[1+\gamma(n-1)]$ times as great as in the case of undivided molecules. If this pressure p is p_0 in the latter case, then

$$p=p_0[1+\gamma(n-1)],$$

wherefore

$$\gamma=\frac{p-p_0}{(n-1)p_0}. \qquad \ldots\ldots\ldots \qquad (1)$$

From the electrical conductivity we are to able find the value of γ in the following way: As the dilution becomes greater, the *molecular conductivity* increases. By this term we mean the specific conductivity of the solution multiplied by the number of liters in which a gram-molecule of the substance is dissolved As the dilution is gradually increased, the molecular conductivity approaches a definite limit. Since the conductivity is only due to the dissociated molecules, it may be assumed that, when this limit is reached, all the molecules are broken up into ions. If the molecular conductivity for infinite dilution is represented by λ_∞ and that for the dilution v (1 gram-molecule in v liters) by λ_v, it is evident that

$$\gamma=\frac{\lambda_v}{\lambda_\infty}. \qquad \ldots\ldots\ldots \qquad (2)$$

The following table shows the agreement of the values calculated by the two methods. The values opposite γ_0 were calculated from the observed freezing-point depressions and those opposite γ_e from the conductivities of the salt solutions. The concentration throughout is 1 g. per liter.

	KCl.	NH_4Cl.	KI.	$NaNO_3$.
γ_0	0.82	0.88	0.90	0.82
γ_e	0.86	0.84	0.92	0.82

66. *Ionic Equilibrium.*—In a case of electrolytic dissociation we have an equilibrium to deal with, namely, that between the undissociated molecules on the one hand and the ions on the other. In the case of a monobasic acid this equilibrium may be represented by

$$AH \rightleftarrows A' + H^{\cdot},$$

where A' is the acid radical (anion) and $H^{\cdot}$ the hydrogen ion (cation). For a base we have

$$MOH \rightleftarrows M^{\cdot} + OH'.$$

We may apply here the equilibrium equation deduced in § 49. Given a gram-molecules of AH per unit-volume, of which x are divided into two ions each, then the equilibrium is represented by

$$a-x=Kx^2.$$

From this equation it necessarily follows that *the dissociation is diminished by the introduction into the solution of a substance with like ions* (just as the addition of hydrogen or iodine reduces the dissociation of hydrogen iodide gas, § 50). This effect may be produced on a salt in solution by the addition to the solution of a salt of the same base or a salt of the same acid. The equation then becomes

$$a-x=K\cdot x(x+p),$$

p being the concentration of the added ion. K can only remain constant provided x diminishes.

It also follows that *the degree of dissociation depends on the concentration.* If the latter be increased n-fold, we have from the above equation

$$n(a-x)=Kn^2x^2, \quad \text{or} \quad (a-x)=K\cdot n\cdot x^2.$$

If n is >1, x must diminish, i.e. *the ionization decreases with increasing concentration.* If n is <1, x must increase, i.e. *the ionization increases with the dilution.* When n is infinitely small, we have $a=x$, in other words, *at infinite dilution the ionization is complete.*

We are now able to give another definition of acids and bases than that of § 30. *Acids are those substances which give H-ions in aqueous solution; bases under the same condition give OH-ions.*

All the properties of acids, bases and salts are closely connected with the degree of their ionization,—among others that which is indicated by the rather vague term *strength of an acid or base.*

As early as the eighteenth century it was observed that an acid can sometimes expel another acid from its salts. On adding hydrochloric acid to sodium carbonate, for instance, sodium chloride is formed and carbonic acid given off. The same is true of bases. When a solution of caustic soda is added to a solution of iron chloride, iron hydroxide is precipitated and sodium chloride is also formed. The acid or base that can expel another from its salts was considered by BERGMANN (1735–1784) to be "stronger" than the one expelled.

Experience has taught that those acids and bases are strongest which are the most ionized for the same dilution. Hydrochloric acid is, for example, stronger than hydrofluoric acid. At a dilution of one gram-molecule per liter the former is almost completely (about 80%) split up into ions, the latter only 3%.

It was remarked above (§ 30) that acids turn blue litmus red, and bases red litmus blue. It is only natural to seek the cause of these common properties of acids on the one hand and bases on the other in that which all acid solutions have in common, namely, hydrogen ions, and in that which all solutions of bases have in common, namely, hydroxyl ions. The reactions between acids, bases and salts in aqueous solution are almost invariably reactions between their ions. We shall explain this later in many instances; the following example may suffice for the present. When dilute solutions of a base and an acid are mixed, we have a salt solution (§ 30). In order to understand what reaction has taken place we must know that in dilute solution most salts are almost wholly split up into ions. Water itself, however, is split up only in an extremely small amount. In the equilibrium

$$H_2O \rightleftarrows H^{\cdot} + OH',$$

there is thus very little of the system on the right-hand side. Now, when a base and an acid are mixed we have together in the solution $M^{\cdot} + OH'$ and $A' + H^{\cdot}$. Of these ions $M^{\cdot}$ and A' can exist freely side by side; but not so with $H^{\cdot} + OH'$, for these must unite to form water according to the above equilibrium. In the formation of the salt we therefore have only the $H^{\cdot}$ and OH' ions uniting, producing undissociated molecules of water.

It is now easy to understand also why a strong acid (i.e. one almost completely ionized) expels a weak (slightly ionized) acid from its salts. To use an example, suppose we add to a liter of a sodium fluoride solution, containing one mole of the salt, a similar solution of hydrochloric acid. In the mixed solution we have the ions

$$H^{\cdot}+Cl'+Na^{\cdot}+F'.$$

Since the equilibrium $HF \rightleftarrows H^{\cdot}+F'$ is conditioned on the presence of only 3% of $H^{\cdot}$ ions and F' ions, there is a large excess of these ions in the liquid and almost all of them must unite with each other, while the $Na^{\cdot}$ and Cl' ions remain free; in other words, hydrofluoric acid and sodium chloride (dissociated) are formed.

It also becomes manifest that the old notion, once very generally held, that the stronger acid expels the weaker one from its salts *completely* is incorrect. When the expelled acid or base escapes from the solution as a gas or is precipitated, the expulsion may indeed seem to be complete; we shall examine the case more thoroughly in § 73.

We can now go a step farther. It was stated above that water is partially ionized, though only to a very slight extent. Suppose that we dissolve in water a salt of a strong base and an extremely weak acid, such as potassium cyanide, for instance. As such a salt is highly ionized, we have in the solution the ions

$$H^{\cdot}+OH'+K^{\cdot}+CN'.$$

Since the acid HCN is very weak, there will be too many CN' ions in the liquid to satisfy the demands of the equilibrium equation

$$H^{\cdot}+CN' \rightleftarrows HCN;$$

hence some of the $H^{\cdot}$ ions of the water will unite with CN' ions. At the same time, however, an excess of OH' ions is created in the liquid; for, inasmuch as potassium hydroxide is a strong base, they do not unite with the $K^{\cdot}$ ions. The water, which originally reacts neutral, because hydrogen and hydroxyl ions are present in equal numbers and are mutually compensating in regard to their action on litmus, thus comes to have an alkaline reaction by the solution in it of potassium cyanide. We therefore see that salts of this nature are partially split up by water into free base ($K^{\cdot}+OH'$) and free acid (undissociated HCN). This phenomenon is called **hydrolysis.** We shall meet with it frequently in the sequel.

When ARRHENIUS presented the doctrine of electrolytic dissociation in 1887, it met with much opposition. It was seen that its effect would be to produce a veritable revolution of many previously accepted views. Compounds such as hydrochloric acid, sodium nitrate and others, which had ever been considered as the most stable, were to be supposed according to the theory of ARRHENIUS to break up as soon as they dissolve in water. It also seemed nonsensical that we should have to assume the existence of free potassium and iodine in a solution of potassium iodide, for example, since potassium produces hydrogen and potassium hydroxide as soon as it touches water and since a KI solution is colorless, while iodine solutions are brown.

So far as the first point is concerned, it should be noted that it is the solutions of these same strongly ionized compounds which are chemically the most active, a fact which indicates rather a loose than a firm union of the constituent atoms in the molecules. In regard to the example of potassium iodide solution and other cases, care must be taken not to confuse atoms and ions. The solution of potassium iodide—retaining our illustration—contains neither free potassium nor free iodine but *ions of potassium* and *ions of iodine.* The atoms, however, must possess an altogether different energy supply than the ions, whose electric charges are very heavy, as can be proved by different methods. It is this *energy supply* on which the properties of bodies depend; and since this is apparently much different with the ions than with the atoms, it is perfectly natural that the latter should display other properties than the former.

SULPHUR.

67. Sulphur was known to the ancients. It occurs free in nature, principally in the vicinity of active or extinct volcanoes. Sicily is its most important locality, closely followed by Louisiana in the United States, but large quantities are also found in other parts of the United States and in Iceland, Japan, and Mexico.

It is separated from the accompanying rock, or matrix, by fusion.

In Louisiana this is accomplished by the FRASCH process, whereby hot water under pressure is forced through pipes sunk through the ground to the sulphur deposit, thus melting the sulphur, which, in a molten form, is forced up to the surface by compressed air.

The crude sulphur thus obtained is still impure. It is refined (Fig. 25) by distillation. After being melted in *B* it is let down into the cast-iron cylinder *A*, which is heated to a temperature above the boiling-point of sulphur. The vapor is conducted into a large brick chamber, equipped with a safety valve for the release of air. If the distillation is conducted so slowly that the temperature of the chamber does not exceed the boiling-point of sulphur, the latter is deposited in the form of a fine powder, called "*flowers of sulphur*"—just as water vapor, when suddenly cooled below 0°, turns to snow. Rapid distillation, however, yields a layer of liquid sulphur on the floor. It may be let out through the opening *C* and cast into slightly conical wooden molds. This is the roll sulphur, or the *roll brimstone*, of commerce.

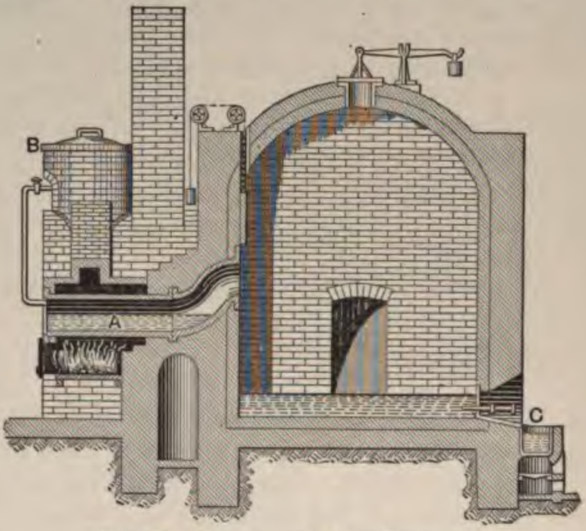


FIG. 25.—DISTILLATION OF SULPHUR.

Besides occurring in the free state sulphur is also found in numerous compounds, from some of which it is obtained, e.g. *pyrite*, or iron pyrites, FeS_2, which yields sulphur on heating:

$$3FeS_2 = Fe_3S_4 + 2S.$$

Many other compounds of the element with metals, the **sulphides**, occur in nature, e.g. *galenite* (lead sulphide), *zinc blende* (sphalerite, zinc sulphide), *stibnite* (antimony sulphide), *cinnabar* (mercury sulphide), *realgar* and *orpiment* (arsenic sulphides) and *chalcopyrite* (copper pyrites, copper and iron sulphide). Sulphur also occurs in the natural sulphates, of which *gypsum* ($CaSO_4+2H_2O$) is the most important. It is also found in the organic world as a constituent of the albuminoids.

Physical Properties.—Sulphur is known in various modifications. At ordinary temperatures the stable form is a yellow crystalline solid; melting-point, 119.25°. A little above its melting-point sulphur is a mobile yellow liquid. With a continued rise of temperature it becomes much darker in color and very viscid; at 180° it can no longer be poured; at a higher temperature, especially above 300°, it again becomes mobile, the dark color remaining; at 448° it boils, producing an orange-colored vapor. At 500° the vapor is red; above this temperature it becomes clearer again. During cooling these phenomena reappear in inverse order. At $-80°$ sulphur is colorless.

Sulphur is insoluble in water and difficultly soluble in alcohol and in ether; it is easily soluble in carbon disulphide and in sulphur monochloride, S_2Cl_2. 100 parts CS_2 dissolve 46 parts S at 22°.

The *molecular weight* of this element, more than that of any other, depends on the temperature. Below the boiling-point the molecular formula is S_8, according to the determination of the boiling-point elevation in carbon disulphide (boiling-point 46°) and the freezing-point depression of fused naphthalene (melting-point 80°). In the gaseous state the density ($air = 1$) varies from 7.937 at 467.9° to 2.23 at 860° and then remains constant even as high as 1800°, indicating that at the lowest temperatures sulphur vapor consists of S_8 molecules, and above 860° of only S_2 molecules.

Above 1800° the molecule S_2 begins to dissociate into its atoms; at 2000° and 0.5 atmosphere pressure the dissociation has reached about 45%, according to an investigation of NERNST.

68. *Allotropic Modifications.*—At least four solid forms are known, while in the liquid state there are two more. The solid allotropic conditions can be divided into crystallized and amorphous. Sulphur is dimorphic, forming *rhombic* as well as *mono-*

clinic crystals. The former are transformed into the latter on heating (§ 70).

Rhombic sulphur can be obtained in beautiful crystals by allowing a solution of sulphur in carbon disulphide or chloroform to slowly evaporate. Monoclinic sulphur is easily obtained in the following manner: Some sulphur is fused in a large crucible and allowed to cool slowly until a crust forms on the surface. The crust is then broken through and the liquid sulphur poured out; the sides of the crucible are found to be covered with long, yellow transparent needles. In the course of a few hours these become opaque and brittle, however, and crumble at the slightest touch to a powder, which is found to consist of rhombic crystals (*cf.* § 71).

Amorphous sulphur may be either soft and soluble in carbon disulphide or powdery and insouble in this liquid.

The soluble kind results from the decomposition of certain sulphur compounds. When hydrogen sulphide water is exposed to the air, sulphur slowly separates in the form of a white powder. The polysulphides (CaS_n, K_2S_n, etc.) yield, when decomposed by an acid, a cloudy milk-like liquid, which is found to contain extremely fine particles of amorphous sulphur. In either case there is always formed in addition to the soluble variety some insoluble (in CS_2) sulphur.

The insoluble form may be best prepared by heating sulphur to near its boiling point and then pouring it in a fine stream into cold water; thereby a semi-solid *plastic* modification is formed, which becomes brittle after a time. By extraction with carbon disulphide the soluble modification is removed and a yellow powder remains, which is the amorphous modification, insoluble in that liquid. The relative quantity of this latter modification depends only on the temperature at which the sulphur was heated. The higher the temperature, the greater the yield; on heating at 440°, for example, the yield is 30.3%. It is a very curious fact that amorphous sulphur is not formed if a few bubbles of ammonia gas or of carbon dioxide are first passed into the heated sulphur and that, on the contrary, the introduction of air will restore the ability to form amorphous sulphur. Probably traces of sulphur dioxide are necessary for the formation of the amorphous state. Further, it has been proved that molten sulphur, no matter whether it can produce the amorphous modification by rapid cooling or not, has in both cases the same physical properties, such as specific gravity, boiling-point, solubility, etc.

In order to explain this fact, the conduct of sulphur on heating must be considered. As has already been stated, sulphur when heated above its melting-point is at first a mobile liquid. When the temperature reaches 160° the liquid very soon becomes viscid. If the temperature is maintained for some time at 158–160°, the molten mass separates into two liquid layers, a mobile one and a viscid one. In other words, sulphur can form two liquid modifications, which are only partially miscible. At every temperature an equilibrium establishes itself in the molten sulphur between these modifications. When rapidly cooled the viscid form continues to exist, for the reason that its transition velocity is strongly diminished, and gives the amorphous modification on solidifying. When cooled slowly the viscid modification changes gradually into the mobile liquid form and the resulting solid does not contain amorphous sulphur. That amorphous sulphur is not obtained by rapidly cooling molten sulphur which is completely free from sulphur dioxide, must probably be attributed to a very strong catalytic retardation of the transition of the viscid form into the mobile one by traces of sulphur dioxide.

69. *Chemical Properties.* — Sulphur combines directly with many elements, not only metals but also metalloids. It has been already stated (§ 10) that it burns with a blue flame when heated in air or in oxygen. The halogens and hydrogen unite with it directly. Powdered iron and sulphur, when mixed and heated, combine energetically, producing great heat (§ 20). Copper takes fire in the vapor of boiling sulphur. When mercury and sulphur are rubbed together in a mortar, black mercuric sulphide, HgS, is formed. The sulphur compounds of the metals are called sulphides.

THE TRANSITION POINT.

70. As stated in § 68 sulphur can crystallize in two modifications, rhombic and monoclinic. These modifications can be readily transformed into one another. The peculiar phenomena connected with this transition deserve a closer study. At ordinary temperatures sulphur is rhombic and remains so till the temperature 95.4° is reached, above which there begins a slow but complete transformation into the monoclinic variety. Inversely, when the monoclinic modification is subjected to a temperature below 95.4°, a complete change into the rhombic form occurs. At the temperature named the two modifications are equally stable and can exist side by side in any proportions for an indefinite period; above it only the monoclinic, below it only the rhombic, form can exist permanently. Such phenomena are not infrequent.

The temperature at which the one system passes into the other is called the **transition point,** also **point of inversion.** This transition point possesses great analogy with the melting-point. Just as ice, for example, is changed into water above 0° and water into ice below 0°, so in a system of substances possessing a transition point only one system is stable below that point, above it only the other.

The theoretical explanation of both phenomena is exactly the same. Let us consider a body, ice for example, at temperatures slightly below its melting-point, and represent graphically in the diagram *OTP* (Fig. 26) the values of the vapor tension corresponding to different temperatures. The result is the line marked *ice* in the figure. This vapor-tension curve, if prolonged through and beyond the melting-point, is found to bend sharply at the latter and take a new direction. This deflection is very slight in the case of ice and water; it can be nevertheless experimentally detected; it is much more evident with benzene and many other substances. By carefully cooling water it can be made to remain liquid even under 0°; such a liquid is said to be supercooled. The vapor tension of this supercooled water is greater than that of ice at the same temperature and the curve representing the former is but a continuation of the vapor-tension curve for water. Since the vapor tension of supercooled water is greater than that of ice, water at temperatures below 0° must, according to previous conclusions (§ 43, 3), pass into ice when the two are in contact. However, the vapor tension of water at a temperature slightly above 0° will be less than that of ice and we shall have the ice transformed into water. It is therefore evident that both above and below the melting-point one of the systems will necessarily disappear.

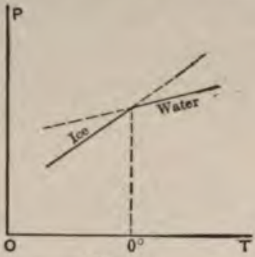


FIG. 26.

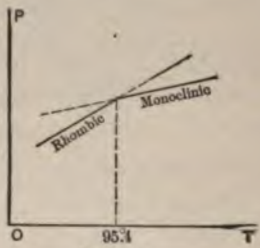


FIG. 27

Exactly the same explanation can be offered for the *transition point*. Below 95.4° the vapor tension of rhombic sulphur is less than that of monoclinic sulphur; above, the vapor tension of the rhombic variety exceeds that of the monoclinic. There is therefore a complete transformation from one system to the other when the temperature is other than 95.4°, for the same reason as in the case of the melting-point; moreover, just as ice and water under ordinary pressure can exist side by side indefinitely only at 0°, so both modifications of sulphur are coexistent only at 95.4°, since only then is the vapor tension the same for both systems (Fig. 27).

Of the various methods for the **determination of the transition point** a convenient one is the *dilatometric method*. It is based on the change of volume (specific gravity) which a body usually undergoes on passing through the transition point. In measuring this a dilatometer is used, an instrument which may be compared to a thermometer of very large dimensions. After rhombic sulphur, for example, has been placed in the dilatometer the latter is filled with a chemically indifferent liquid (kerosene, linseed oil) and put in a large water bath; the temperature is then slowly raised. Below the transition point the volume is seen to slowly and steadily increase with the temperature on account of expansion; as soon as the temperature gets a trifle above 95.4°, however, a marked increase of volume is observed, even if the temperature be maintained constant; thereupon expansion again proceeds gradually, as before, if the temperature is allowed to rise. The marked change of volume indicates the transition of the rhombic sulphur into the monoclinic modification.

THE PHASE RULE OF GIBBS.

71. The *phase rule* treats of the **equilibrium in heterogeneous systems,** i.e. systems that can be separated mechanically into unlike parts. A saturated salt solution in contact with solid salt is a heterogeneous system, for it consists of solid salt, the solution and vapor; that is, of three parts, mechanically separable. Each of these parts in itself is homogeneous, i.e. each part has the same composition throughout. A gas mixture is always homogeneous, as is also a solution. These homogeneous parts, separated by limiting surfaces and of which a heterogeneous system is made up, are called by Gibbs **phases.** Water and its vapor constitute two phases; ice, water and steam three phases.

A heterogeneous system can never have more than one gaseous phase, because all gases are miscible in all proportions; it may, however, consist of different liquid phases, in case it contains immiscible liquids. The number of these liquid phases is seldom more than two; that of the solid phases is unlimited.

A further conception, introduced by Gibbs, is that of the **components** of a system. If the system is composed of only one element, then this element is the only component. Systems made up of one compound have in most cases this compound as the only component. A system consisting of molten and gaseous sulphur, or of water and steam, has but one component. In this case all phases have the same composition. There are systems, however, in which this is not the case; viz. systems that are made up of more than one component. We select as the components those compounds of which the smallest number is necessary to form the different phases. The choice of such compounds may be somewhat arbitrary but their *number* is always fully defined.

Let us consider, for example, the system Glauber's salt-water. This salt has the composition, $Na_2SO_4 \cdot 10H_2O$. In order to determine the composition of the phases that are possible here (solid salt, solution, vapor) it is best to choose Na_2SO_4 and H_2O as components. We might indeed take Glauber's salt itself as one of the components; but then, in case the solid phase was the anhydrous salt, it would be necessary to regard water as a negative part of it, which is undesirable. Sulphuric acid and sodium hydroxide are not components, because they do not occur independently in any phase, neither are they found in any other relation in the phases than as a part of the salt itself. It is a property of the components that they can occur in some of the phases in varying proportions (e.g. in saturated and unsaturated solutions).

Let us now take, for example, a saturated solution of salt and water in a vessel that is closed with a movable piston. Under this solution let there be a little solid salt, above it the vapor of the solution. The system consists manifestly of two substances and three phases.

So long as the temperature remains constant, the vapor of the salt solution possesses a definite tension. If we increase the volume by raising the piston, a definite amount of water will evaporate; since the solution was saturated, the result will be that a little salt will be deposited; in the end the quantities of vapor, solution and salt will therefore have altered, but the composition of each phase will remain the same. The tension, and hence also the concentration, of the vapor remain unchanged, since the temperature is constant; there is likewise no change in the concentration of the salt solution. The same is true in case the volume be diminished. It therefore follows that the equilibrium of such a system is independent of the quantities of the various phases. It is dependent only on the temperature chosen; if this is constant, the whole system is defined. Or, if we should select an arbitrary value for the composition, the temperature and pressure would be fully defined. It is therefore evident that the system is completely defined as soon as one of these magnitudes is arbitrarily chosen. The system has only one **degree of freedom.** Such an equilibrium possesses the following characteristic: At a given constant temperature the vapor pressure is definite. Under an even slightly greater or smaller pressure one of the phases will gradually and completely disappear, provided the temperature remains constant. On increasing the pressure the gaseous phase wholly condenses, so that only solution and salt remain. A decrease of pressure results in the complete evaporation of the solution, vapor and salt only being left.

The same is true when the pressure remains constant and the temperature varies.

An entirely different behavior is shown by a system made up of an unsaturated salt solution and its vapor. At a constant temperature and a definite position of the piston the vapor tension has a definite value, as in the former case. If, however, the volume of vapor be changed, the tension will correspondingly vary, for, if the volume be increased, for example, more water will evaporate, the solution will become more concentrated and the vapor tension of course lessen. Therefore for every definite temperature there are not simply one but infinitely many pressures under which this system can be in equilibrium. The result is that the slightest change of volume or pressure does not necessitate the disappearance of one of the phases. Two magnitudes may be chosen arbitrarily before the system is fully defined; it has two degress of freedom. It is evident in this example that the number of degrees of freedom increases by one when the number of phases decreases by one.

The phase rule expresses a relation between the numbers of the components S, the phases P, and the degrees of freedom F. It is of the following form:

$$F+P=S+2,$$

or, in words, *The sum of the number of the degrees of freedom and the number of the phases of a system exceeds the number of components by two.*

Let us apply the phase rule in the first place to water, a system of one component; the sum of the degrees of freedom and the phases must therefore be three.

In the following graphic representation, Fig. 28, the temperatures, t, are plotted as abscissæ, the pressures, P, as ordinates. Let us first consider liquid water above 0°. The number of the phases is two (liquid and vapor); the system has therefore only one degree of freedom, or, as we say, it is **univariant.** To every temperature there corresponds a definite vapor tension. The ordinates of every point in the line OB indicate these vapor ten-

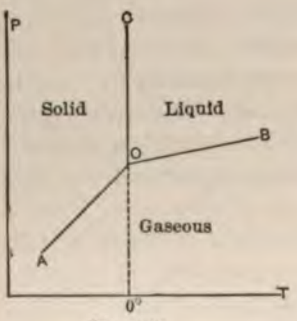


FIG. 28.

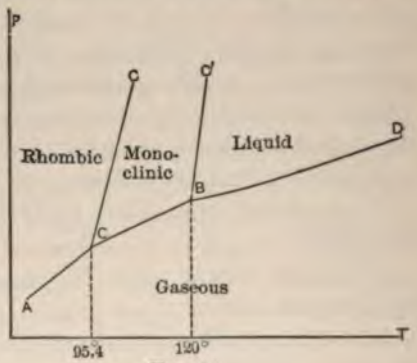


FIG. 29.

sions. If the pressure at a certain temperature were greater than that indicated by the ordinate, the gaseous phase would completely disappear. The line *OB* therefore represents the boundary between the liquid and gaseous phases for the various temperatures and pressures. Every point in the area *COB* represents the liquid, every point in *AOB* the gaseous, phase. Only the points of the line *OB* indicate the temperatures and corresponding pressures, at which both phases are coexistent. The line *OB* therefore ends on one side at 0°; its other end is at the critical temperature, since at this point vapor and liquid become identical.—Let us now allow the temperature to fall below 0°. The liquid phase disappears and ice takes its place. The system remains unvariant, however, for the number of phases is unchanged. The ordinates of the points on the line *OA* again give the vapor tensions of ice for different temperatures. For the same reason as above *OA* is the boundary line between the solid and gaseous phases. Only along this line are the two coexistent. The line *OA* extends to the absolute zero, since the gaseous phase then disappears.

The melting-point of ice depends somewhat on the pressure, being lowered by increasing pressure 0.0075° per atmosphere. Both phases, ice and water, will therefore be coexistent along the line *OC*, which shows a very considerable rise of pressure for a very slight fall of temperature. In this case also a change of pressure at a constant temperature, or the reverse, involves the complete disappearance of one of the phases. The line *OC* will end at a point where the liquid and solid phases become identical, i.e. where the whole system turns to a homogeneous amorphous mass. The location of this point has not yet been ascertained.

The point *O*, the melting-point of ice, is, according to the above mode of representation, the point of intersection of the three lines which separate the phases and along which two phases are coexistent. It is called a **triple point.** Only in this point is it possible for the *three* phases to exist side by side; it is the common point of the areas which represent regions of the three phases. When three phases are coexistent the system has no degree of freedom; it has become **non-variant.**

In the case of sulphur we have one substance and four possible phases: rhombic, monoclinic, liquid, gaseous. Fig. 28 makes plain the relation between these phases. Below 95.4° sulphur is rhombic; the two phases are rhombic sulphur and vapor. The line OA forms the boundary between the two regions. At 95.4° the rhombic phase passes into the monoclinic phase. The ordinates of the line OB represent the vapor pressure of monoclinic sulphur at the temperatures 95.4°–120°. The two crystallizable phases can exist side by side at the point O (the transition point). According to researches by REICHER this transition point depends on the pressure; an increase of pressure of one atmosphere raises it about 0.05°. The boundary between the crystallized phases is therefore furnished by a line OC, which shows that a very slight rise of temperature is followed by a very considerable increase of pressure. At O we have therefore a triple point, i.e. a point common to both crystallized phases and the gaseous phase. At B, the melting-point of monoclinic sulphur, there is a second triple point, which is wholly analogous to the melting-point of ice. Finally, it should also be noted that the line BC', which separates the liquid and the solid phases, must indicate a rise of melting-point for an increase of pressure, since sulphur melts higher the greater the pressure. The lines OC and BC' are not parallel but intersect, according to TAMMANN's experiments, at 151° and 1281 atmospheres. As the sum of the phases and degrees of freedom is also three with sulphur, the phase rule indicates that all four phases cannot exist in the presence of each other at the same time, not even when the system has become non-variant.

At the triple point neither the temperature nor the pressure can be changed without altering the kind of equilibrium. Here the system is *non-variant*. Along the lines OA, OB and OC it is *univariant*. When the state of the system is represented by a point within one of the areas it is *divariant*, consisting then of only one phase. In the succeeding chapters we shall have occasion to concern ourselves with systems of more than one component.

HYDROGEN SULPHIDE, SULPHURETTED HYDROGEN, H_2S.

72. This gas occurs in nature chiefly in volcanic regions. Certain mineral waters, especially the so-called "sulphur springs," contain it. It is also found as a putrefactive product of organic bodies.

Hydrogen sulphide can be obtained from its elements by synthesis. They unite almost completely when heated together for a long time (about 168 hours) at 310°.

It can also be obtained by the action of hydrogen on sulphur compounds, as well as by the action of sulphur on compounds of hydrogen; the reduction of silver sulphide, Ag_2S, with hydrogen at high temperatures illustrates the former case, while the boiling of turpentine oil with sulphur is an example of the latter.

None of the above methods is adapted to the preparation of the gas in the laboratory. For this purpose the interaction of a sulphide with a hydrogen compound is employed, iron sulphide and dilute acids being generally used:

$$FeS + 2HCl = FeCl_2 + H_2S.$$

In order to have sulphuretted hydrogen always at hand, it being in constant demand in analytical work (*cf.* § 73), a very convenient apparatus was devised by KIPP, which can be used for the generation (at ordinary temperatures) of other gases as well. Its construction is shown in the figure (see next page).

The lower globe is joined to the basal portion by a narrow neck, while the upper globe tapers into a long tube, which fits tightly into the lower globe and extends nearly to the bottom of the generator without completely filling the neck. The iron sulphide is put into the middle portion and the dilute acid is poured into the upper portion, the stopcock remaining open. As soon as the basal part is filled with the acid the cock is closed and the top part is half filled with more acid. When the cock is opened the liquid sinks in the top part and rises into the middle portion, where it reacts with the iron sulphide to produce hydrogen sulphide, which escapes through the cock. On closing the latter the gas continues to be evolved till it forces the liquid back out of the part containing the iron sulphide. The reaction thus ceases automatically and the generator is ready at any time to supply new quantities of gas on opening the cock, till either acid or sulphide is exhausted. The spent acid can be let out through a stoppered opening near the bottom.

On account of the free iron usually present in iron sulphide, the gas prepared in this manner contains some hydrogen. Perfectly pure hydrogen sulphide is obtained by warming antimony sulphide, Sb_2S_3, with concentrated hydrochloric acid.

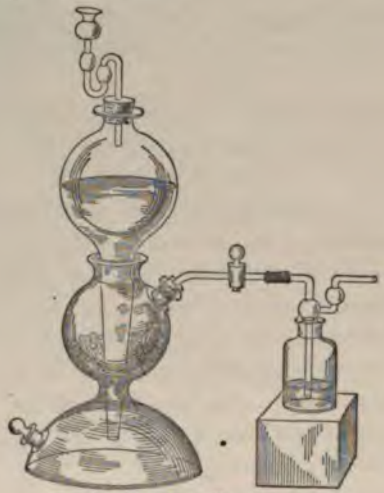


FIG. 31.—KIPP GENERATOR.

Physical Properties.—Hydrogen sulphide is a colorless gas of disagreeable odor, when diluted reminding one of rotten eggs. Under a pressure of about 17 atmospheres it becomes liquid at ordinary temperatures; liquid hydrogen sulphide boils at −61.8° and freezes at −85°. The gas is rather soluble in water, 1 vol. water dissolving 4.37 vols. H_2S at 0° ("hydrogen sulphide water"). It is poisonous; as an antidote very dilute chlorine may be inhaled.

Chemical Properties.—Hydrogen sulphide is combustible and yields on combustion either sulphur dioxide and water or water and sulphur, according to the air supply:

$$H_2S+3O=H_2O+SO_2; \quad H_2S+O=H_2O+S.$$

In aqueous solution it is slowly oxidized by the oxygen of the air, sulphur being set free; this decomposition is aided by light. In order to preserve hydrogen sulphide water, it must be prepared from boiled (air-free) water and put into a dark bottle, filled entirely and closed air-tight. The latter condition is best met by placing the bottle, stopper downwards, in a glass of water.

Hydrogen sulphide is a powerful reducing-agent. Bromine water and iodine solution are decolorized by it with separation of sulphur (§§ 45 and 48).

Various oxygen compounds are transformed by hydrogen sulphide into compounds with less oxygen, e.g. chromic acid is reduced in acid solution to a chromic salt (§ 295). Fuming nitric acid acts so vigorously that a slight explosion occurs. When hydrogen sulphide is passed over lead dioxide, the gas ignites, while the oxide is reduced. Concentrated sulphuric acid, H_2SO_4, is also reduced; hence it cannot be used for drying the gas.

Hydrogen sulphide possesses the character of a weak acid; when it is passed over zinc, copper, tin or lead, the corresponding sulphides are formed and hydrogen is set free.

Composition of Hydrogen Sulphide.—When a bit of tin is heated in dry hydrogen sulphide—in a tube over mercury—tin sulphide and hydrogen are formed. After cooling it is seen that the volume of hydrogen is just as great as that of the hydrogen sulphide. The same result is obtained when a platinum wire is heated to redness (by an electric current) in the dry gas, causing the latter to break up into its elements. Since the hydrogen molecule is H_2, there must be two atoms of hydrogen in the hydrogen sulphide molecule. Now the specific gravity of hydrogen sulphide has been found to be 1.1912 for air = 1, or 17.15 for O = 16. The gram-molecule therefore weighs 34.30 g., and, as it contains 2 g. hydrogen, there remains for sulphur 32.3 g. This figure is very close to the atomic weight of sulphur, hence there can only be one atom of sulphur present in the molecule of hydrogen sulphide. We thus conclude that the formula is H_2S.

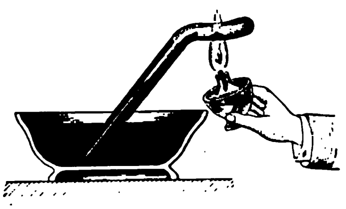


FIG. 32.—DECOMPOSITION OF H_2S.

73. *Use of Hydrogen Sulphide in Analysis.*—Hydrogen sulphide finds extensive use in qualitative analysis. A large number of metals are precipitated by it from acid solutions as sulphides, viz., gold, platinum, arsenic, antimony, tin, silver, mercury, lead, bismuth, copper and cadmium, and also certain rare elements. Some of these sulphides have a characteristic color, e.g. the orange-red antimony sulphide, Sb_2S_3, the yellow cadmium sulphide,

CdS, the brown stannous sulphide, SnS, the yellow stannic sulphide, SnS_2, and the yellow sulphides of arsenic, As_2S_3 and As_2S_5. The rest of the sulphides named are black. Other metals, such as nickel, cobalt, iron, manganese, zinc, chromium, aluminium, etc., are not precipitated by hydrogen sulphide from acid solution but are precipitated by ammonium sulphide. Still other metals, such as barium, strontium, calcium, magnesium, and the alkalies, are not precipitated from their solutions even by ammonium sulphide, so that we therefore possess in sulphuretted hydrogen and its ammonium compound a means of separating these elements.

An answer to the question, why some elements are precipitated from acid solution by hydrogen sulphide and others are not, is furnished by the ionic theory. Let us take, for example, a dilute solution of copper sulphate, into which hydrogen sulphide is being passed. Copper sulphate is almost entirely ionized, hydrogen sulphide only to a very small degree (∂). We therefore have in the solution:

$$Cu^{\cdot\cdot}+SO_4''+2\partial H^{\cdot}+\partial S''+(1-\partial)H_2S,$$

the cations being represented by a point and the anions by a line above and to the right, and the number of these points or lines indicating the ionic valence (§ 76).

Some of the copper ions and sulphur ions will then unite to form undissociated molecules, CuS, which are only slightly soluble in water and are therefore precipitated. As S-ions thus disappear, the equilibrium between hydrogen sulphide and its ions is disturbed; new H_2S molecules are then split up into ions, so that there are again S-ions present, which can unite with copper, and so on. The action proceeds according to the equation:

$$CuSO_4+H_2S=\underset{\text{Insol.}}{CuS}+H_2SO_4,$$

or, if only the ions which take part in it are represented:

$$Cu^{\cdot\cdot}+S''=CuS.$$

This takes place quantitatively if the copper solution is dilute and no considerable amount of any strong free acid was added. However, if these conditions are not fulfilled and, as a result, the concentration of the hydrogen ions is rather high, the presence of these ions reduces the ionization of H_2S so much (§ 66) that no precipitate can be formed. The application of the mass-action law to the case is very simple. Copper sulphide, when in contact with water, dissolves to an extremely small extent; in this solution we have the equilibrium:

$$Cu^{\cdot\cdot} + S'' \rightleftarrows CuS.$$

If the concentrations of the two ions are a and b, and that of the undissociated copper sulphide is c, we have the equation

$$ab = k \cdot c,$$

k being a constant for a fixed temperature (§ 66).

The product ab has a definite value for every saturated solution (since c is definite). This value is known as the **solubility product** of the substance in question. If in any case the product ab is less than this value, none of the substance can separate out, because the solution will then be unsaturated; if, however, the product is greater than the solubility product, the substance will be precipitated.

As soon then as the concentration of the S-ions becomes so small (because of the reduction of the ionization of hydrogen sulphide by the H-ions of the acid) that it makes the value of ab smaller than that of the solubility product for copper sulphide, no precipitate will be formed. If, however, the liquid is diluted, the concentration of the H-ions decreases; then, if hydrogen sulphide is passed in, the concentration of the S-ions increases. The value of the solubility product can in this way be exceeded, in which event copper sulphide will be precipitated.

If a small quantity of strong acid be added to a precipitate of copper sulphide suspended in water, only a very small amount of the sulphide will dissolve; to be sure, the H-ions of the strong acid will remove a part of the S-ions, yielding some undissociated hydrogen sulphide, so that in order to establish equilibrium a trace of copper sulphide must go into solution; but soon the point will be reached when so many Cu- and S-ions are again in the solution that the value of the solubility product is reached. After this moment no more copper sulphide goes into solution. Since the value of the solubility product is very low, the solubility of the sulphide in dilute strong acids is very slight; this accounts for the practically complete precipitation of the copper sulphide.

On the other hand, if the solubility product of a sulphide is greater, as in the case of iron sulphide, the addition of sulphuretted hydrogen to the solution of an iron salt, e.g. ferrous sulphate, $FeSO_4$, will cause no precipitate of iron sulphide, and iron sulphide will, unlike the previous case, be dissolved by dilute strong acids. When hydrogen sulphide is led into a solution of ferrous sulphate to the point of saturation, the concentration of the S-ions is, on account of the slight ionization of hydrogen sulphide, not great enough together with that of the Fe-ions to reach the solubility product of iron sulphide, hence no precipitate forms. Moreover, when dilute hydrochloric acid is added to iron sulphide, the H-ions and the S-ions form undissociated H_2S molecules and the concentration of the S-ions therefore becomes too small in comparison with the value of the solubility product to prevent solution; hence in the presence of enough acid all the iron sulphide goes into solution.

It now becomes clear, too, why iron solutions are precipitated by ammonium sulphide. This takes place according to the equation

$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4.$$

In this case there are no H-ions in the solution to act on the iron sulphide.

The reason for the non-precipitation of metals like barium, etc., either by sulphuretted hydrogen or ammonium sulphide lies in the easy solubility of their sulphides.

Hydrogen Persulphide.

74. On boiling a solution of a base, potash or lime, with sulphur, polysulphides are formed, i.e. compounds like K_2S_2, K_2S_3, etc., up to K_2S_5 or CaS_5. When a solution of these substances is treated with hydrochloric acid, a dense oily liquid, hydrogen persulphide, separates out, whose composition is approximately represented by the formula H_2S_5. It is, however, very unstable; it can not, for instance, be distilled, even in a vacuum.

Compounds of Sulphur with the Halogens.

75. If chlorine is conducted over molten sulphur **sulphur monochloride,** S_2Cl_2, is formed. Its formula is based on its vapor

density and analysis. It is a yellow liquid of a very disagreeable, pungent odor, which excites one to tears. It boils at 139° and possesses in a high degree the ability to dissolve sulphur—as much as 66% at ordinary temperatures. This solution is a thick syrupy liquid. It is used in the vulcanizing of rubber.

Sulphur monochloride is slowly decomposed by water:

$$2S_2Cl_2+2H_2O=SO_2+3S+4HCl.$$

Two other compounds of sulphur and chlorine are known, SCl_2 and SCl_4.

Sulphur dichloride, SCl_2, is formed, slowly, when sulphur monochloride is mixed with liquid chlorine. The mixture has a yellow color at first but after a few days it turns red. A determination of the vapor density of the red substance and of its lowering of the freezing-point of acetic acid or benzene leads to the formula SCl_2. It should, however, be borne in mind that a mixture of sulphur monochloride and chlorine, $S_2Cl_2+Cl_2$, must give the same molecular weight as the compound SCl_2. The existence of the SCl_2 compound is proved not only by the above-mentioned change of color of mixtures of sulphur monochloride and chlorine but also by the following observations: (1) The composition of the vapor given off from fresh mixtures of sulphur monochloride and chlorine is entirely different from that of the vapor given off after the mixture has turned red. (2) Mixtures of sulphur monochloride and chlorine decrease in volume, and this diminution is greatest when the composition corresponds to $S_2Cl_2+Cl_2$. (3) The freezing-point curve of the system:—sulphur and chlorine—also indicates the existence of SCl_2 (§ 237, 2).

With **bromine** and **iodine** sulphur gives analogous compounds.

Sulphur tetrachloride, SCl_4, crystallizes in very small crystals when mixtures of sulphur monochloride and chlorine that have stood for a long time are cooled down by liquid air. Its melting-point is about $-30°$. No one has yet succeeded in isolating the crystals from the liquid in which they are formed; nevertheless the form of the freezing-point curve of these mixtures indicates unquestionably the formula SCl_4 for the crystals. *Cf.* § 237.

Fluorine unites with **sulphur** to form a gas of the formula SF_6 and of rather surprising properties. It is colorless, odorless and incombustible. At $-55°$ it solidifies with the formation of crystals.

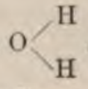
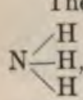
Notwithstanding its high percentage of fluorine it is chemically so indifferent that it almost resembles nitrogen in this respect (see p. 163). For instance, it is not decomposed by fused alkalies nor by copper oxide at dull-red heat. It can be heated with hydrogen without yielding hydrogen fluoride. Moreover, sodium can be fused in sulphur hexafluoride without losing its metallic surface, the gas not being attacked by the metal till the boiling-point of the latter is reached.

VALENCE.

76. Certain elements have the property whereby their atoms can combine with only one atom of another element. The halogens on the one hand and hydrogen on the other are able to form only compounds of the type HX(X=halogen). This property of the atoms is called **univalence.**

In the case of other elements like oxygen and sulphur each atom can enter into compounds with two univalent atoms (examples: H_2S, H_2O). These are therefore called **bivalent.**

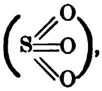
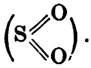
The number of univalent atoms that can combine with one atom of a given element serves in an analogous way as a measure of valence in general. An atom of nitrogen, for instance, unites with three atoms of hydrogen; nitrogen is therefore trivalent; carbon is quadrivalent, etc.

The valence is ordinarily indicated by lines, as in  $\mathrm{O}\begin{matrix}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{matrix}$ and  $\mathrm{N}\begin{matrix}\diagup \mathrm{H}\\ -\mathrm{H}\\ \diagdown \mathrm{H}\end{matrix}$, each line representing a valence unit (unit bond).

The valence of one and the same element may be different according to the nature of the univalent elements with which it combines. Sulphur, for instance, can only unite with two hydrogen atoms, but with univalent chlorine it forms the compound SCl_4, with fluorine even SF_6. The valence of sulphur in these cases is therefore four and six. The preparation of sulphur compounds with *more* than six univalent atoms has not yet been accomplished; hence its **maximum valence** is six.

The halogens are univalent towards hydrogen, but in relation to each other they display more than one valence, as may be seen from the compounds ICl_3 and ICl_5; in the compound Cl_2O_7 (§ 60) the maximum valence of chlorine can even be assumed to be seven.

It has been very generally observed that when the maximum valence of an element is an even or an uneven number, its lower valences are of the same sort; the halogens and sulphur illustrate this. However, these are exceptions to this rule.

The valence also depends upon the temperature. We shall soon see that SO_3 dissociates at a high temperature into SO_2 and oxygen; while sulphur is sexivalent towards oxygen at lower temperatures , it is only quadrivalent towards oxygen above 700° . The valence must also depend on the pressure, for the latter exerts a great influence on the dissociation.

The basis for the above sort of formulæ is the idea, borrowed from organic chemistry, that the atoms of a molecule may not assume any conceivable arrangement whatsoever, but that there is a definite order in every molecule.

For some extensions of the idea of valence see § 317.

Valence of Ions.—In the solution of an electrolyte the sums of all the positive and all the negative amounts of electricity must be equal, for the solution acts as electrically neutral. In a solution of hydrochloric acid the positive charge of the H-ions must be numerically equal to the negative charge of the Cl-ions and, since the same number of both ions are present, each Cl-ion must carry a charge equal, but opposite in sign, to that of an H-ion. In a sulphuric acid solution, however, the two H-ions together must possess just as much positive electricity as the SO_4-ion negative electricity. The SO_4'' ion is therefore called bivalent in respect to the hydrogen ion. It is readily seen how the valence of other ions can be determined in an analogous manner, for it is equal to the numerical value of their electrical charge, that of the hydrogen ion being taken as unity.

Compounds of Sulphur with Oxygen.

77. Of those containing only the two elements four are known, viz., S_2O_3, SO_2, SO_3 and S_2O_7. Especial importance attaches itself, however, only to SO_2 and SO_3; the two others have been little studied.

Sulphur Sesquioxide, S_2O_3.

This is obtained when sulphur is treated with its trioxide. It is a blue liquid, which congeals to a malachite-green mass and is soluble in fuming sulphuric acid, giving a blue solution. On being warmed it breaks up into sulphur and the dioxide:

$$2S_2O_3 = 3SO_2 + S.$$

Water decomposes it with the formation of sulphur, sulphurous acid and polythionic acids.

SULPHUR DIOXIDE, SULPHUROUS ANHYDRIDE, SO_2.

78. This gas occurs in nature in volcanic gases. It is formed when sulphur burns in the air or in oxygen; the well-known odor of burning sulphur is due to it. A little trioxide is also formed by this combustion. The laboratory method of preparation consists in decomposing sulphuric acid with copper.

$$2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O.$$

For this purpose concentrated sulphuric acid is heated with copper turnings, no action taking place at ordinary temperatures. The process can be explained by supposing that at the high temperature of the reaction copper is oxidized by sulphuric acid to copper oxide with the evolution of sulphur dioxide:

$$Cu + H_2SO_4 = SO_2 + H_2O + CuO.$$

The copper oxide reacts of course with a second molecule of sulphuric acid, producing copper sulphate.

The reduction of concentrated sulphuric acid by heating with charcoal is also a convenient method of preparation:

$$2H_2SO_4 + C = 2H_2O + 2SO_2 + CO_2.$$

However, as this equation shows, the gas is obtained mixed with one third of its volume of carbon dioxide, from which it cannot be separated directly.

Moreover, sulphur dioxide can be obtained by the action of oxygen on sulphur compounds, thus, e.g. by the roasting of pyrite in a current of air:

$$\underset{\text{Pyrite.}}{FeS_2} + 3O_2 = SO_2 + FeSO_4.$$

This reaction is employed on a large scale in the commercial manufacture of sulphuric acid.

The action of sulphur on oxygen compounds also yields sulphurous oxide, e.g. heating copper oxide or manganese dioxide with sulphur:

$$2CuO + 2S = Cu_2S + SO_2; \quad MnO_2 + 2S = MnS + SO_2.$$

Finally, the dioxide is also formed by heating an oxygen compound (CuO) with a sulphur compound (CuS):

$$CuS + 2CuO = 3Cu + SO_2.$$

Physical Properties.—At ordinary temperatures and pressures sulphur dioxide is a gas. It has a peculiar taste and odor. It is easily liquefied, the boiling-point being $-8°$. Its evaporation produces a marked depression of temperature, sometimes extending to $-50°$; at $-76°$ it becomes solid. Liquid sulphur dioxide dissolves many salts, in some cases with a characteristic color. It is very soluble in water; at 0° 1 vol. H_2O dissolves 79.79 vols. SO_2, at 20° 39.37 vols. SO_2. Boiling the solution expels all the gas (§ 84).

Chemical Properties.—Sulphur dioxide is an acid anhydride; its aqueous solution has an acid reaction and behaves in general like that of an acid (§ 84). It is easily oxidized by oxidizing-agents to the trioxide. This occurs, for instance, when a mixture of sulphur dioxide and air or oxygen is passed over hot spongy platinum or platinum asbestos. In aqueous solution this oxidation takes place readily at ordinary temperatures. The oxidation of the dioxide can also be brought about by chlorine-water, bromine and iodine:

$$Cl_2 + 2H_2O + SO_2 = H_2SO_4 + 2HCl;$$

also by chromic acid, which is reduced to chromium sulphate, or by potassium permanganate, which is reduced to a mixture of manganese and potassium sulphates, and therefore loses its color:

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

Lead peroxide glows faintly in a current of sulphur dioxide and is reduced to lead sulphate—from brown to white:

$$PbO_2+SO_2=PbSO_4.$$

It is to its reducing action that the bleaching effect of sulphurous oxide on vegetable coloring-matters is due. A red rose, for example, loses color in it. The gas probably reacts with water, setting hydrogen free, which latter effects the reduction and hence the bleaching:

$$SO_2+2H_2O=H_2SO_4+H_2.$$

In this case, therefore, bleaching depends on a reduction; as a matter of fact the color returns in many instances, when the bleached article is exposed to the oxidizing action of the air. Silk, wool and straw, i.e. substances that cannot stand the chlorine bleaching, are whitened commercially with sulphurous oxide. It also finds use as an antiseptic.

The reduction of iodic acid by sulphur dioxide is sometimes employed as a test for the latter. For this purpose strips of paper are dipped in a solution of potassium iodate and starch, which turns blue in the presence of sulphur dioxide—iodine being set free (§ 47).

If the reaction is carried out in dilute solution, a peculiar phenomenon is observed; the blue color of starch iodide does not appear directly when the solutions of sulphur dioxide and iodic acid are mixed, but is withheld for a certain number of seconds (definite for every concentration at constant temperature), when it suddenly appears. The following reactions come into play:

$$\text{I. } 3SO_2aq+HIO_3=3H_2SO_4aq+HI.$$

The hydriodic acid thus formed is at once oxidized by the iodic acid still present:

$$\text{II. } 5HI+HIO_3=3H_2O+6I.$$

So long as sulphur dioxide is present, it reduces the iodine in this dilute solution to hydriodic acid:

$$\text{III. } 2I+SO_2aq+2H_2O=H_2SO_4aq+2HI.$$

Not until all the dioxide is used up by the reactions I and III does the free iodine suddenly appear according to II.

There are some substances which are able to extract oxygen from sulphur dioxide, i.e. the latter can also act as an *oxidizing-agent.* Ignited magnesium ribbon continues to burn in sulphur dioxide, forming magnesium oxide and sulphur. Hydrogen sulphide and sulphur dioxide have respectively an oxidizing and a reducing effect on each other, which follows mainly the equation:

$$2H_2S + SO_2 = 2H_2O + 3S.$$

Sulphur dioxide is decomposed by electric sparks into sulphur and the trioxide.

The action of the electric sparks is to be ascribed solely to the sudden and enormous rise of temperature which they produce and the rapid cooling that immediately follows, for the gas particles which have become heated by the sparks are immediately cooled again by surrounding objects. As a result the products formed do not have time to react in the opposite direction. The correctness of this view was demonstrated by St. Claire Deville with the help of an apparatus which made it possible to cool objects very rapidly from a very high temperature. This apparatus, the cold-hot tube, consists of a rather wide porcelain tube, which is heated to a bright glow in a furnace and which contains a concentric thinner metallic tube, through which cold water is forced so rapidly that the tube maintains a low temperature. When Deville introduced sulphur dioxide into the space between the two tubes, it was seen after some time that the inner tube, which was made of silver-plated copper, had turned black because of the formation of silver sulphide, while at the same time the formation of sulphur trioxide could be detected (by its producing sulphuric acid with water, a precipitate being given by barium chloride).

The *composition* of sulphurous oxide can be determined in the following manner: When sulphur burns in oxygen no change of volume is observed after cooling. Therefore just as many molecules of sulphurous oxide have been formed as oxygen molecules consumed. The sulphurous oxide molecule must therefore contain two atoms of oxygen. The specific gravity of the gas has been found to be 2.2639 (air = 1), or 32.6 (O = 16), so that its molecular weight is 65.2. If we subtract 2×16 from this for two atoms of oxygen, there remains 33.2 for sulphur, the atomic weight of which is 32. We thus see that only one atom of sulphur is present in the molecule of sulphurous oxide and that the formula of the latter is SO_2.

SULPHUR TRIOXIDE, SULPHURIC ANHYDRIDE, SO_3.

79. This compound is found in a small amount in the fumes of burning sulphur (§ 78). As was stated above, oxygen and sulphur dioxide unite to form the trioxide in the presence of platinized asbestos. A similar contact action is produced by iron oxide, Fe_2O_3, chromium oxide, Cr_2O_3, and a few other substances. Upon this phenomenon is based a commercial process for the manufacture of sulphur trioxide (see § 86). The catalytic action of the above substances must be explained as in the previous cases of catalysis (§ 49); that is, by considering that sulphur dioxide and oxygen unite without the catalyzer, but only very slowly (the formation of a small amount of the trioxide on burning sulphur is evidence of this), and that the action of the catalyzer simply consists in accelerating the process.

Sulphur trioxide can also be obtained by heating certain sulphates; in the arts ferric sulphate is thus used:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

"Fuming sulphuric acid" (oleum) is a solution of sulphur trioxide in sulphuric acid; the anhydride can be obtained from it by distillation.

Physical Properties.—Perfectly dry sulphur trioxide melts at 17.7° and boils at 46°. It looks much like ice but usually appears in another modification, viz., long asbestos-like needles with a silky lustre. These crystals have no sharp melting-point but sublime on heating. This modification is the stable one, for the other goes over into it spontaneously. This transformation is greatly accelerated by traces of water. The asbestine modification consists of double molecules $(SO_3)_2$, the glacial form of simple molecules (SO_3). This is shown by the depression of the freezing-point of phosphorus oxychloride. The first is therefore called a *polymer* of the second. It is also worth noting that the SO_3 modification is very readily soluble in concentrated sulphuric acid, while the other, $(SO_3)_2$, dissolves with difficulty.

Chemical Properties.—Sulphur trioxide unites very easily with water to form sulphuric acid:

$$SO_3 + H_2O = H_2SO_4.$$

It therefore fumes vigorously when exposed to moist air. On introducing it into water, combination and great evolution of heat, accompanied by sizzling, results. It reacts energetically with many metallic oxides also, forming sulphates. Baryta, for example, glows in contact with it. When its vapor is passed through a red-hot tube, it is decomposed into the dioxide and oxygen.

Composition.—The decomposition just mentioned permits us to establish the composition of sulphuric oxide. The dissociation products, SO_2 and O_2, are formed in the volume ratio 2:1. Now the specific gravity of sulphuric oxide is 2.75 (air = 1), from which the molecular weight is calculated to be 79.1. This figure corresponds to the formula $SO_3(32+3\times16)$ and it also harmonizes with the above dissociation; for it is clear that 2 vols. SO_3 must then yield 2 vols. SO_2 and 1 vol. O_2:

$$\underset{\text{2 vols.}}{2SO_3} = \underset{\text{2 vols.}}{2SO_2} + \underset{\text{1 vol.}}{O_2}.$$

Sulphur Heptoxide, S_2O_7.

80. This compound is formed when a mixture of equal volumes of dry oxygen and sulphur dioxide is subjected to a dark electric discharge of high potential. It consists of oily drops which crystallize below 0° and break up slightly above that temperature into trioxide and oxygen. With water it forms sulphuric acid and oxygen:

$$4H_2O + 2S_2O_7 = 4H_2SO_4 + O_2.$$

Oxygen Acids of Sulphur.

81. Sulphur forms an unusually large number of acids with oxygen and hydrogen, namely nine. They are as follows:

1. Thiosulphuric acid	$H_2S_2O_3$.
2. Hyposulphurous acid	$H_2S_2O_4$.
3. Sulphurous acid	H_2SO_3.
4. Sulphuric acid	H_2SO_4.
5. Persulphuric acid	$H_2S_2O_8$.
6. Dithionic acid	$H_2S_2O_6$.
7. Trithionic acid	$H_2S_3O_6$.
8. Tetrathionic acid	$H_2S_4O_6$.
9. Pentathionic acid	$H_2S_5O_6$.

It is an important fact, however, that of these nine acids only sulphuric acid has really been isolated; all the others are known only in aqueous solution or in the form of salts. The two hydrogen atoms which each of these acids possesses are both replaceable by metals; they are therefore *dibasic* acids. With such acids it is possible that just one of the hydrogen atoms be replaced by a metal. The salts thus formed are called **acid salts.**

By different methods, e.g. the cryoscopic method, it is found that the aqueous solution of dibasic acids AH_2 contains chiefly the ions $H^{\cdot}$ and HA'; it is only when these solutions are very dilute that the anion HA' splits up further into $H^{\cdot}$ and A''. In the case of the M_2A salts, however, there is an ionization into $2M^{\cdot}+A''$; but in that of the acid salts MHA the ions are chiefly $M^{\cdot}$ and HA'. How far the anion HA' is split up does not depend merely on the concentration, but also to a considerable degree on the strength of the acid, HA' being more ionized in strong than in weak acids of the same concentration.

THIOSULPHURIC ACID, $H_2S_2O_3$.

82. This acid can only exist in dilute aqueous solution and is even then very unstable, decomposing completely in a short time. The salts are, however, stable and can be prepared in the following ways:

1. By boiling the solution of a sulphite with sulphur;

$$\underset{\text{Sodium sulphite.}}{Na_2SO_3}+S=Na_2S_2O_3;$$

or

$$SO_3''+S=S_2O_3'',$$

only the anion being changed.

2. By the oxidation of sulphides in the air;

$$\underset{\text{Calcium disulphide.}}{2CaS_2}+3O_2=2CaS_2O_3.$$

3. By the action of sulphur dioxide on the solution of a sulphide:

$$4Na_2S+6SO_2=4Na_2S_2O_3+S_2.$$

The most important salt is the sodium thiosulphate, formerly and even yet often called sodium hyposulphite, or, abbreviated, "hypo." It is very soluble in water; the solution, when used in excess, has the property of dissolving readily the halogen compounds of silver, hence its extensive use in photography (§ 247). It is easily oxidized by oxidizing-agents, usually to the sulphate. This takes place with potassium permanganate, nitric acid and chlorine, for example. Practical use is also made of this latter property by employing sodium thiosulphate as an *antichlor* in bleaching, i.e. to remove the last traces of chlorine which cling to the bleached material very obstinately and have an injurious effect.

When a dilute acid is added to a dilute solution of sodium thiosulphate, the following decomposition takes place:

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 + S;$$

or

$$S_2O_3'' + 2H^{\cdot} = \underset{\text{Anion of sulphurous acid.}}{HSO_3'} + H^{\cdot} + S.$$

It may be, however, that the ions first unite partially to form $H_2S_2O_3$, which splits up into H_2O, S and SO_2.

It is an interesting fact that in this decomposition in a dilute solution the sulphur precipitate is not at once visible, being first noticeable after some seconds, or even minutes, according to the dilution. It was formerly supposed that the thiosulphuric acid remained entirely unchanged until the appearance of the sulphur and the decomposition first began at this moment. This is, however, incorrect; for when a dilute solution of thiosulphate is treated with an equivalent amount of dilute acid and the solution again neutralized before the appearance of the sulphur deposit, it is found that the latter appears nevertheless after some time. A certain part of the free thiosulphuric acid must therefore have already decomposed, but the sulphur was in a so very finely divided state in the liquid that it could not at once be detected,—not until it had gathered together to form larger particles.

Hyposulphurous Acid, $H_2S_2O_4$.

83. As early as the 18th century it was observed that zinc is dissolved by a solution of sulphur dioxide in water without the evolution of hydrogen. SCHÜTZENBERGER was, however, the first to show that a particular acid is formed thereby. A salt of this acid is produced by the action of zinc on a solution of acid sodium sulphite, $NaHSO_3$, or by the electrolysis of such a solution, the nascent hydrogen acting as a reducing-agent.

Hyposulphurous acid, as well as its salts, is characterized by a vigorous reducing power. It precipitates the metals from solutions of sublimate ($HgCl_2$), silver nitrate and copper sulphate. Iodine solution is bleached by it with the formation of hydrogen iodide; indigo is reduced to indigo-white. The solution is also very easily oxidized by free oxygen. It is therefore used to determine the amount of oxygen dissolved in water. For this reason it must be kept in well-stoppered vessels.

Bernthsen succeeded in preparing the solid sodium salt, which proved to have the composition $Na_2S_2O_4+2H_2O$, so that the acid itself has the formula $H_2S_2O_4$. This salt was isolated by preparing a concentrated solution of it and precipitating it by the addition of a suitable amount of solid common salt. The above formula is also confirmed by a direct synthesis of the sodium salt by Moissan, who obtained it by the action of dry sulphur dioxide on sodium:

$$2Na+2SO_2=Na_2S_2O_4.$$

SULPHUROUS ACID, H_2SO_3.

84. It is taken for granted that the aqueous solution of sulphur dioxide contains sulphurous acid, H_2SO_3, for this solution reacts acid, conducts the electric current, gives salts with bases and evolves hydrogen with some metals, e.g. magnesium. The solution of sulphur dioxide in water does not conform to the law of Henry (§ 9) at ordinary temperatures, which proves that a combination with the solvent has taken place. At higher temperatures, however, the solution obeys this law pretty well. A fact in confirmation of this is that all the sulphur dioxide can be expelled from the solution by boiling it, the combination being then wholly destroyed. The compound H_2SO_3 itself has, however, not yet been isolated. The salts have the composition M_2SO_3 and $MHSO_3$ (M being an atom of a univalent metal). The acid salts are almost all soluble in water, while of the neutral salts only those of the alkalies are soluble. The acid sodium sulphite, $NaHSO_3$ (sodium bisulphite), is frequently employed in organic chemistry. Sulphites in solution gradually absorb oxygen from the air, forming sulphates. It is a very strange fact that minute quantities of organic substances, e.g. only 0.1% of alcohol and as little as 10^{-5} gram molecule of stannous chloride, greatly hinder this oxidation. We have here one of the few examples of a retarding catalytical action. On the other hand, traces of copper sulphate considerably accelerate the oxidation.

SULPHURIC ACID, H_2SO_4.

85. Sulphuric acid is the most important acid of sulphur. It can be obtained in varoius ways; in the first place by direct synthesis from its elements. According to § 79 sulphur trioxide can be formed directly from sulphur and oxygen, and this yields sulphuric acid on the addition of water.

The acid can be obtained from its salts by distilling them with phosphoric acid. Its formation from the action of oxygen on sulphur compounds is illustrated by the oxidation of an aqueous SO_2-solution by the air. On the other hand the action of sulphur on oxygen compounds may also give sulphuric acid; thus it is formed when concentrated nitric acid, HNO_3, is boiled with sulphur; and again, potassium sulphate is formed by heating sulphur with saltpetre (KNO_3).

86. For the *commercial manufacture* of sulphuric acid two processes are now in use, the lead-chamber process and the contact process. Enormous amounts of the acid are produced by these two methods.

The lead-chamber process is based on the following reactions: 1. the oxidation of sulphur dioxide by nitric acid in the presence of water; 2. the oxidation by the oxygen in the air of lower oxides of nitrogen formed from the nitric acid in the previous reaction. These are partly reconverted to nitric acid and partly changed to certain stages of oxidation of nitrogen which oxidize sulphur dioxide anew to sulphuric acid. By this last process the lower nitrogen oxides are again formed, but are soon reoxidized by atmospheric oxygen and so on. One might suppose that a certain amount of nitric acid would suffice to convert unlimited amounts of sulphur dioxide into sulphuric acid with the aid of the air. In practice this is not true, however; for the nitrogen oxides are to a small extent still farther reduced by sulphurous oxide, so that nitrous oxide or nitrogen are formed, and these are no longer able, under the conditions of the industrial process, to combine with oxygen.

As may be seen from the above, the chemical process which lies at the basis of the manufacture of sulphuric acid is a very complicated one. As a matter of fact it has not yet been possible to explain it fully. In the main it takes the following course.

I. Sulphur dioxide is oxidized to sulphuric acid by nitric acid in the presence of water:

$$3SO_2+2HNO_3+2H_2O=3H_2SO_4+2NO.$$

The nitric oxide (NO) thus formed is again oxidized by oxygen and water to nitric acid:

$$2NO+3O+H_2O=2HNO_3.$$

II. However, the nitric oxide may absorb oxygen according to a still different reaction:

$$NO+O=\underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{NO_2}.$$

This nitrogen dioxide also has the ability to oxidize sulphur dioxide with the re-formation of nitric oxide:

$$SO_2+H_2O+NO_2=H_2SO_4+NO.$$

III. Sulphur dioxide and nitric acid, or sulphur dioxide, nitrogen dioxide, oxygen and water, can react with each other so that a crystallized compound, **nitrosyl sulphuric acid,** $SO_2OH(ONO)$ ("lead-chamber crystals"), are formed. These are decomposed by water into $NO+NO_2$ and sulphuric acid:

$$SO_2+HNO_3=SO_4H(NO);$$
$$2SO_2+NO_2+NO+O_2+H_2O=2SO_4H(NO);$$
$$2SO_4HNO+2H_2O=2SO_4H_2+2HNO_2;$$
$$2HNO_2=NO+NO_2+H_2O \text{ (cf. § 126).}$$

From a technical standpoint the lead-chamber process falls into three separate parts:

1. The preparation of sulphur dioxide;
2. The oxidation of sulphur dioxide;
3. The concentration of the resulting acid.

(1) The material for the production of the dioxide is sulphur or pyrite (iron pyrites, FeS_2). Sulphur yields a purer acid than pyrite; that prepared from the latter almost always contains arsenic. The roasting of the pyrite is carried on in furnaces, the construction of which varies considerably. In all of them, however, the sulphur dioxide leaves the furnace mixed with a good deal of air. The furnace gases pass through a canal in which the dust particles carried along by the draught are deposited.

(2) The oxidation of the sulphurous acid is carried out in a structure (Fig. 33) consisting chiefly of three parts, the Glover

tower, *A*, the lead chambers, *B*, *B'*, *B''*, and the Gay-Lussac tower, *C*.

The **Glover tower** is made of sheet lead lined with acid-proof brick. It is filled with lump stone over which is laid a layer of smaller pieces of coke. On top of the tower is a reservoir for collecting the nitroso sulphuric acid (see below) that comes from the Gay-Lussac tower and the lead chambers and is to be concentrated in the Glover tower. It flows down over the stone in the tower from a horizontally revolving tube.

The **lead chambers** are three or four in number and have a total capacity of 4000–5000 cubic meters. Their form is that of a parallelopiped, whose cross-section is nearly a square. The length is either the same in all or it gradually increases from the first to the last. Lead has been chosen as the material for the walls of the chambers, because it is the only one of the common metals which is only slightly attacked by sulphuric acid and the substances used in its manufacture.

The lead chambers are connected with each other, with the Glover tower and with the Gay-Lussac tower by means of lead tubes so attached that the gases have to enter the upper part of the chamber and depart at the bottom, or *vice versa*. In the first two chambers, preferably near the tubes which supply the gases, but in other places as well, tubes are also introduced to conduct steam from the boilers, *DD*.

The walls of the **Gay-Lussac tower** are likewise of lead. Here, however, it does not have to be protected by fire-brick, since the temperature of the gases coursing through the tower is not so high. Usually it is entirely filled with coke. On top of the tower is a reservoir containing 60°–62° sulphuric acid (BAUMÉ, see § 88), which comes from the Glover tower.

Let us now examine the task that befalls each of these three—the Glover tower, the Gay-Lussac tower and the lead chambers.

The gases that come from the pyrite furnace consist of a mixture of sulphur dioxide and air, a larger proportion of the latter than is required for the oxidation. They have a temperature of about 300°, when they enter the Glover tower, *A*, at the opening, *w*. The gas current rising in the tower meets an acid mixture flowing down from above. The latter consists of the nitroso acid from the Gay-Lussac tower, diluted with the acid (*chamber acid*)

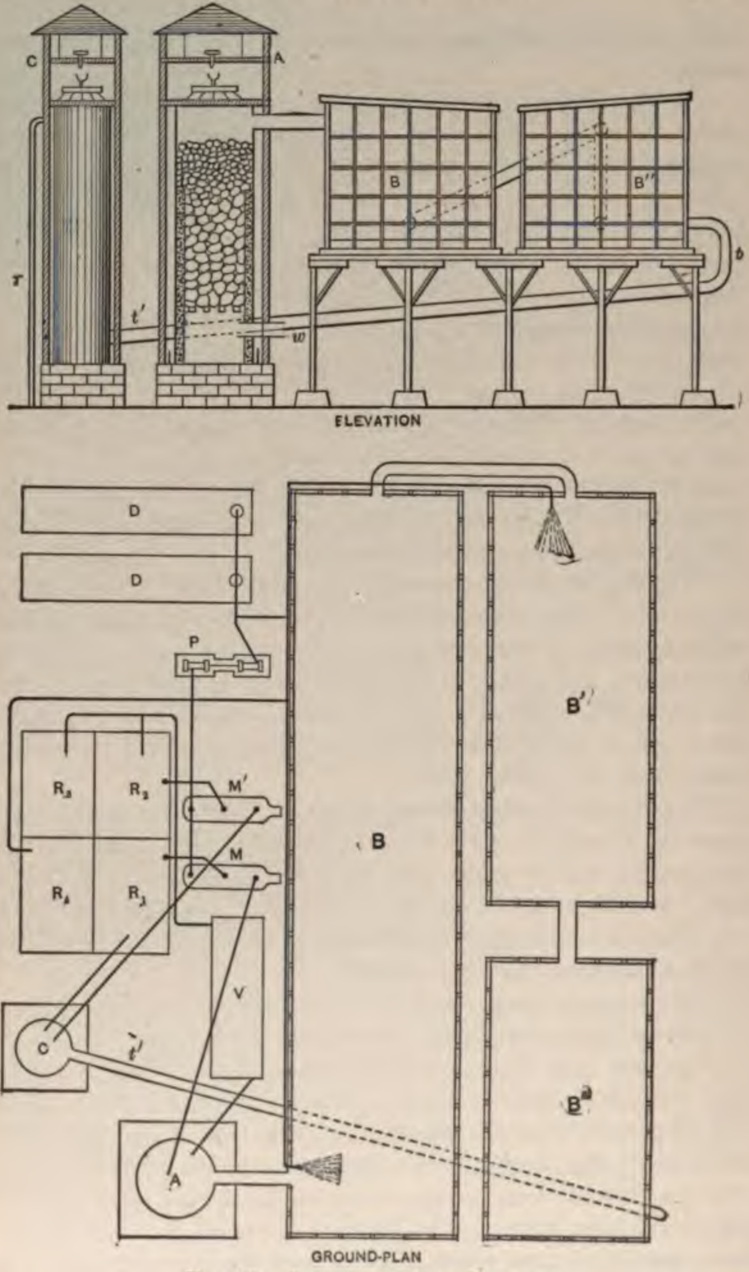


Fig. 33.—Sulphuric Acid Factory.

The terms: *B*, *B'*, *B''*, Lead chambers; *C*, Gay-Lussac tower; *A*, Glover tower; *D*, Water boiler; *r*, Pipe to chimney; *tt'*, Pipe from third chamber to Gay-Lussac tower.

which collects in the lead chambers, and a little nitric acid—this latter to replace the nitrogen oxides lost in the process. By means of the Glover tower the following is accomplished: In the first place, the acid which flows out from the tower contains only traces of nitroso products (§ 128); these are volatilized and carried off with the hot gases coming from the pyrite furnace. In the second place, the sulphuric acid is deprived of some of the water with which it was diluted, the water being carried off as steam by the passing gas current. The acid has a concentration of 60°–62° BAUMÉ at the bottom. In the third place, the gases are cooled down to 60°–80° during the passage through the tower, and arrive at the top of it in just the right condition for the formation of sulphuric acid; the Glover tower therefore yields a quantity of acid equal to at least one-tenth of the product formed in the chambers.

From the Glover tower the gas mixture, now consisting of nitrogen oxides, steam and sulphurous oxide, goes to the first chamber, in which, as well as in the second, the above reactions are carried out. The third chamber serves principally to cool and dry the gases before they reach the Gay-Lussac tower; on this account, moreover, it is not supplied with a steam pipe.

When the gases leave the third chamber, they still contain nitroso products, which cannot be allowed to escape without loss. The Gay-Lussac tower serves for the purpose of retaining these by letting them dissolve in 62° BAUMÉ acid. The gases are led in at the bottom of the tower through the tube, *tt'*; they give up their nitrogen oxides to the sulphuric acid with which the coke piled up in the tower, as above described, is coated, and escape through the tube, *r*, which opens into the great chimney. By means of the latter a powerful draft is maintained throughout the entire plant.

(3) The acid produced in the chambers contains about 67% H_2SO_4 (53° BAUMÉ). In this condition it is employed directly in the manufacture of fertilizers ("superphosphate"). For almost all other purposes it must first be concentrated. Ordinary sulphuric acid of commerce is of about 66° B. (B. = BAUMÉ), i.e. 96–98% H_2SO_4. It is prepared from the chamber acid by evaporating it first in lead pans to about 78% (60° B.) and finally in a platinum vessel.

This crude sulphuric acid of commerce ("oil of vitriol") still contains various impurities and is usually more or less brown in color because of bits of straw (from the packing of the carboys) falling in and charring. It can be purified by diluting it, whereupon the dissolved lead sulphate is precipitated, and then stirring in a little barium sulphide. The latter produces insoluble barium sulphate, and also hydrogen sulphide, which precipitates any arsenic or lead (§ 206) still present. The acid is then decanted from the deposit, concentrated, and finally distilled.

The contact process.—It has already been stated that sulphur dioxide unites with oxygen directly to form the trioxide and that the combination is considerably accelerated by the catalytic influence of platinized asbestos. This simple reaction is the basis of the "contact process." In practice, however, air is used instead of pure oxygen.

The process falls into four separate parts: 1. The preparation of a mixture of sulphur dioxide and air; 2. The purification of this mixture; 3. The formation of the trioxide; 4. The combination of sulphur trioxide with water to form sulphuric acid.

(1) The purification of the gas mixture is much the same as in the lead-chamber process. For reasons which will soon be made clear it is found necessary to conduct the roasting in the presence of a large excess of oxygen. While the equation

$$2SO_2+O_2=2SO_3$$

demands only 1 vol. O_2 for each 2 vols. SO_2, the gases are usually mixed in the ratio of 3 vols. O_2 to 2 vols. SO_2.

(2) The platinized asbestos acts efficiently only when the furnace gases are absolutely pure, i.e., when the mixture consists simply of sulphur dioxide and air. The complete purification of these gases has been a problem of exceptional difficulty, but has been accomplished through the perseverance of KNIETSCH of the "Badische Anilin- und Sodafabrik," the great chemical factory at Mannheim, Germany. In the first place the furnace gases must be wholly freed from dust, else the catalyzer would soon become so coated as to lose its activity. In order to determine when the gas is really dust-free it is subjected to the "optical test," i.e., it is passed through a tube closed at both ends with glass, and is

examined with the eye to see whether it is perfectly transparent and free from nebulous masses. Even when this optical test is quite satisfactory the catalyzer suffers a loss in activity if the gas is not entirely free from arsenic compounds; the least traces of the latter have an injurious effect. The presence of arsenic compounds in the furnace gas is due to the occurrence of arsenic in the pyrites (§ 86, 1) used for roasting. KNIETSCH has finally succeeded in completely eliminating the arsenic compounds by blowing steam into the gas mixture.

(3) Since sulphur trioxide dissociates at a high temperature into the dioxide and oxygen, the formation of it from these two gases is a reversible process:

$$2SO_2 + O_2 \rightleftarrows 2SO_3.$$

If the pressure of the dioxide in the state of equilibrium is represented by p_1, that of the oxygen by p_2, and that of the trioxide by p_3, the equilibrium equation must be:

$$p_1^2 p_2 = K p_3^2,$$

where K stands for the equilibrium constant. According to this equation the formation of sulphur trioxide is more complete in the presence of an excess of either sulphur dioxide or oxygen, for as p_1 or p_2 increases p_3 must also increase. Since the object in view is to convert the dioxide as completely as possible into the trioxide, it is advantageous to provide a large excess of oxygen. This explains why more than the theoretical amount of oxygen is taken. Compare (1).

The equilibrium must also depend on the pressure, for, if this is increased n times, the equation becomes:

$$(np_1)^2 np_2 = Kn^2 p_3^2, \quad \text{or} \quad np_1^2 p_2 = K p_3^2,$$

from which it is evident that at a higher pressure ($n > 1$) the formation of the trioxide is more nearly complete (§ 102, 5). The manufacturer does not find it necessary, however, to employ high pressure, which would involve, moreover, a great complication of the apparatus.

Finally, the influence of temperature must be mentioned. Sulphur dioxide unites with oxygen easily at 400°. When equilibrium is established in the system $2SO_3 \rightleftarrows 2SO_2 + O_2$ at this temperature, the left-hand side predominates. If the temperature is raised, the quantity of trioxide formed diminishes, at first slowly, but between 600° and 800° more rapidly, until at 1000° the dissociation of sulphur trioxide is complete and it can no longer be formed. These temperatures hold for a mixture of sulphur dioxide and so much air that the relation $SO_2 : O_2$ is as 2:3, assuming that the pressure is the ordinary one.

If it is desired that the combination of sulphur dioxide and oxygen should be as complete as possible, the temperature must be kept at about 400°. Since, however, the heat of formation of the trioxide is great, viz.,

$$SO_2 + O = SO_3 + 22{,}600 \text{ Cal.},$$

the apparatus must be cooled. This is done most practicably by the aid of a fresh portion of the gas mixture, as the next paragraph sets forth.

The construction of the apparatus is as follows: The tubes *ab* contain the platinized asbestos *b*, supported on little sieves (shown in the middle tubes). The purified furnace gases first pass around the outside of the tubes and are thus warmed to the desired temperature at the heat expense of the gas system within. When the proper temperature is reached the gases are allowed to enter the tubes, where sulphur trioxide is formed with the evolution of more heat. By increasing or diminishing the rate of flow of the gas current the temperature can be regulated very satisfactorily. When the operation is started the apparatus must first be warmed to 400°.

(4) The reaction between sulphur trioxide and water is an energetic one. Nevertheless, the manufacture of sulphuric acid from these two compounds involved some difficulty, inasmuch as sulphur trioxide fumes invariably escaped when this substance was introduced into water or dilute sulphuric acid. Only when sulphuric acid of 97–98% is used as the absorbent and care is taken to keep the acid at this concentration by the simultaneous addition of water does a complete and immediate absorption occur.

This is due to two circumstances: first that traces of water change sulphur trioxide into the asbestine modification (§ 79), which is only slowly absorbed by sulphuric acid; second, that at the concentration of 97–98% H_2SO_4 the system xSO_3+yH_2O has a minimum of vapor tension, which is very low.

87. *Physical Properties.*—The pure compound, hydrogen sulphate, is an oily liquid at ordinary temperatures, solidifying at a low temperature and melting again at +10.0°. Its specific gravity in the liquid state (15°) is 1.8500.

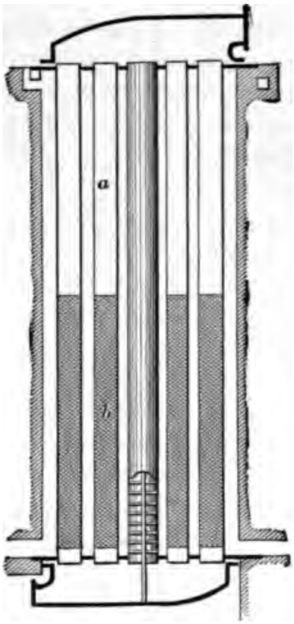


FIG. 34.—CONTACT-PROCESS APPARATUS.

Chemical Properties.—The concentrated acid obtained by distillation is not the simple compound H_2SO_4, for it still contains about 1.5% of water. In order to prepare the absolutely pure acid the distilled product must be mixed with the theoretical amount of sulphur trioxide. When pure sulphuric acid is heated, it begins at 30° to give off fumes of sulphur trioxide; this continues until the boiling-point, 317° at 750 mm. Hg. pressure, is reached, when an acid with 1.5% water distils over. On heating the vapor of sulphuric acid above the boiling-point, it begins to break up into water and the anhydride; this dissociation is complete at

450°, for the vapor density at that temperature is found to be 25.1, while that of SO_3+H_2O is theoretically 24.5.

When sulphuric acid is mixed with water, a strong evolution of heat occurs. The mixing must therefore be done with great care, particularly in glass vessels, the acid being poured in a fine stream into the water and the liquid being steadily stirred. On mixing them in the reverse way, by pouring the water into the sulphuric acid, the intense heat that is produced may cause the glass to crack. However, when the acid is mixed with ice in a certain proportion, a strong cooling follows.

The mixing of sulphuric acid and water is attended by a contraction, i.e. the volume of the dilute acid is smaller than the sum of the volumes of water and acid. It is known that sulphuric acid is able to form hydrates with water (§ 237).

Sulphuric acid is a strong dibasic acid, but not as strong as hydrochloric acid, for, while the latter is ionized to 95% at a dilution of 0.1 gr. mol. per l., sulphuric acid at the same dilution is only ionized to 55% into $2H^{\cdot}+SO_4''$. At higher concentrations HSO_4' ions also exist. It acts on many metals, giving off hydrogen. This action is made use of, as stated above, in the preparation of hydrogen; the acid must, however, be dilute, for when it is too strong or warmed, the hydrogen generated partially reduces the sulphuric acid so that the gas given off contains hydrogen sulphide. Sulphur dioxide also is formed when hydrogen is led into hot sulphuric acid. It is upon this action that the reaction of copper with hot concentrated sulphuric acid depends (§ 78). Mercury, silver and certain other metals are similar to copper in their behavior. Platinum and gold are not attacked by the acid.

Sulphuric acid makes holes in paper, linen, dress goods and the like, when dropped on them. It has a destructive, charring effect on organic substances in general. This is due in many cases to the great tendency of the acid to unite with water, which makes it not only deprive other substances of the water they contain, but even withdraw the hydrogen and oxygen from organic compounds to form water. On the other hand, sulphuric acid gives up oxygen to many organic substances, being itself reduced.

In order to detect free sulphuric acid in vinegar, for example, the liquid is evaporated on a water-bath with a little sugar. Free sulphuric acid, if present, chars the sugar during the concentration.

The most of the salts of sulphuric acid (sulphates) are soluble in water. Barium, strontium, and lead sulphates are insoluble, while calcium sulphate (gypsum) is slightly soluble, but only to a very small degree. The formation of barium sulphate, $BaSO_4$, serves as a *characteristic test for sulphuric acid*, or, as we may better say, for the *ion* SO_4''.

The sulphates are in general very stable. They can, for instance, be heated to very high temperatures without decomposition. The acid salts lose water on heating, and pass over into pyrosulphates:

$$2NaHSO_4 = H_2O + \underset{\text{Sodium pyrosulphate.}}{Na_2S_2O_7}.$$

If these pyrosulphates are heated still higher, they give off sulphur trioxide and form neutral salts:

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

88. *Uses.*—Sulphuric acid is of enormous practical value, its uses being most varied. It is employed in the preparation of almost all other mineral acids from their salts. In the manufacture of soda after LE BLANC it is used in astonishingly large amounts and in nearly all other branches of chemical industry it is of some service or other. In the laboratory it is often employed as a drying-agent. A moist substance is dried very thoroughly when placed in a closed apparatus near a dish of the concentrated acid. For this purpose special pieces of apparatus are constructed, called *desiccators*.

The *determination of the concentration* of sulphuric acid is an operation that is frequently necessary. Ordinarily the specific gravity is made use of, for this can be determined rapidly with an areometer. There are tables so prepared that the proportion of H_2SO_4 or SO_3 in a dilute acid whose specific gravity and temperature are known can be quickly read. BAUMÉ, a chemist of the latter part of the eighteenth century, constructed an areometer with an arbitrary scale, the zero point of which indicates pure water and the point 10 being reached in a 10% salt-solution. All the divisions are equal. 100% H_2SO_4 would then be represented by the line 66.6. In the arts the strength of sulphuric acid is still given as so many "degrees BAUMÉ."

Fuming Sulphuric Acid.

89. This is the name of a sulphuric acid that contains sulphur trioxide in solution. It is obtained by dissolving the oxide in concentrated sulphuric acid.

Fuming sulphuric acid is a thick oily liquid, which fumes vigorously in the air, throwing off the trioxide. Sp. g. = 1.85–1.90. On cooling it **pyrosulphuric acid** ($H_2S_2O_7 = H_2SO_4 + SO_3$) crystallizes out. Some salts of the latter are also known (§ 87). It forms large colorless crystals, that melt at 35°. Pyrosulphuric acid dissociates even at ordinary temperatures, and on gently warming breaks up completely into sulphuric acid and trioxide. Besides pyrosulphuric acid several other compounds of water and sulphur trioxide are known.

CHLORIDES OF SULPHURIC ACID.

90. When phosphorus pentachloride acts on sulphuric acid a compound SO HCl, **chlorosulphonic acid,** is formed:

$$H_2SO_4 + PCl_5 = SO_3HCl + POCl_3 + HCl.$$

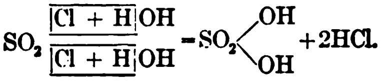
The same compound results from the direct union of sulphur trioxide and hydrochloric acid. It is a colorless liquid, which fumes vigorously on exposure to the air. Sp. g. = 1.766 at 18°. Boiling-point, 158°. On the addition of water a violent reaction occurs, producing hydrochloric acid and sulphuric acid:

$$SO_3HCl + H_2O = H_2SO_4 + HCl.$$

A compound, SO_2Cl_2, **sulphuryl chloride,** is obtained by the direct union of sulphur dioxide and chlorine, most easily by first saturating camphor with sulphur dioxide (which readily dissolves in it) and then passing chlorine over it. The camphor remains unchanged. Sulphuryl chloride is a colorless liquid, which boils at 69.1°, has a penetrating odor, fumes strongly in the air and has a specific gravity of 1.6674 at 20°. The addition of a little water converts it into chlorosulphonic acid and hydrochloric acid, much water to sulphuric and hydrochloric acids:

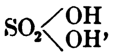
$$SO_2Cl_2 + H_2O = SO_3HCl + HCl.$$
$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

These decompositions of sulphuryl chloride can be represented in the following way:



$$SO_2\begin{array}{|l}\hline Cl + H|OH \\ \hline Cl + H|OH \\ \hline\end{array} = SO_2\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix} + 2HCl.$$

In the place of the two chlorine atoms we have, therefore, two OH (*hydroxyl*) groups entering. For this reason it is assumed, in close analogy with the methods of organic chemistry, that sulphuric acid contains two hydroxyl groups. From this it follows that the arrangement of the atoms in the molecule of sulphuric acid may be represented by the diagram:



$$SO_2\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix},$$

in which the SO_2 (*sulphuryl*) group is joined to two hydroxyls. Such a diagram is known as a **structural,** or **constitutional, formula.**

Sulphuryl fluoride can be obtained by the direct union of sulphur dioxide and fluorine. It has the same remarkable stability as the compound SF_6 (§ 75). It is a colorless and odorless gas, liquid at − 52° and solid at − 120°. It can be heated with water in a sealed tube to 150° without undergoing decomposition. Alkalies absorb it, though very slowly. Sodium can be fused in it without being attacked.

Persulphuric Acid, $H_2S_2O_8$.

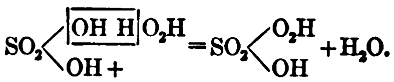
91. The potassium salt, $K_2S_2O_8$, of this acid can be obtained by the electrolysis of a cold saturated solution of potassium sulphate, K_2SO_4, in sulphuric acid of 1.3 sp. g. In such a solution we may assume we have the ions $K^{\cdot}$ and HSO_4'; the latter are discharged at the anode and can then unite to form $H_2S_2O_8$, which forms with the $K^{\cdot}$ ions present the difficultly soluble potassium salt $K_2S_2O_8$; this separates out as a white crystalline mass. However, the combination of two HSO_4 groups only takes place when their concentration at the anode is quite high; for if this is not the case there is more opportunity for secondary reactions, such as a union with water to form $2H_2SO_4$ and 2OH, the latter of which is decomposed into H_2O and O. Such a high concentration at the anode is reached by using a very small electrode. The electric current therefore has a high density at the anode, that is, a large quantity of electricity must pass through a small surface. The effect thereof is that this large quantity discharges a great many HSO_4' ions into a small space, or in other words, produces enough HSO_4 groups to make the concentration very high there. As low as 100° it decomposes in the following way:

$$2K_2S_2O_8 = \underset{\text{K-pyrosulphate.}}{2K_2S_2O_7} + O_2.$$

The barium salt of persulphuric acid is soluble in water, as are also most of the other known salts. The solution of potassium persulphate in sulphuric acid is called **Caro's** *liquid.* It probably contains a compound $H_2SO_5\left(=SO_2<\begin{matrix}OH\\ O_2H\end{matrix}\right)$, which is formed by the action of water on persulphuric acid:

$$HO\cdot SO_2\cdot O-O\cdot SO_2\cdot OH+H_2O=\underset{\text{sulphuric acid}}{HO\cdot SO_2\cdot OH}+\underset{\text{sulphomonoper-acid}}{HO_2\cdot SO_2\cdot OH}.$$

A liquid with the same reactions is obtained by mixing hydrogen peroxide with an excess of strong sulphuric acid:



$$SO_2<\begin{matrix}\boxed{OH\ H}O_2H\\ OH+\end{matrix}=SO_2<\begin{matrix}O_2H\\ OH\end{matrix}+H_2O.$$

This compound is called by **Baeyer** sulphomonoper-acid; it has very strong oxidizing powers. It sets iodine free from potassium iodide, oxidizes sulphur dioxide to trioxide, and ferrous to ferric salts and also precipitates the higher oxides of silver, copper, manganese, cobalt and nickel from solutions of salts of these metals. On the other hand, it neither bleaches permanganate solution nor oxidizes solutions of chromic and titanic acids; in these respects it is distinguished from hydrogen peroxide, to which it otherwise shows much similarity.

POLYTHIONIC ACIDS.

92. Under this name are grouped four acids of the general formula $H_2S_nO_6$, in which the number of sulphur atoms, n, can be 2, 3, 4 and 5, and this determines the names of the individual acids.

Dithionic acid, $H_2S_2O_6$. The manganese salt of this acid is obtained when finely powdered manganese dioxide is suspended in water and sulphurous oxide passed in:

$$2SO_2+MnO_2=MnS_2O_6.$$

From this barium salt the dithionic acid can be liberated by sulphuric acid. The solution can be concentrated *in vacuo* over sulphuric acid till its specific gravity reaches 1.347; farther concentration or warming results in a decomposition:

$$H_2S_2O_6=H_2SO_4+SO_2.$$

Trithionic acid, $H_2S_3O_6$. Potassium trithionate is formed when a solution of potassium thiosulphate is saturated with sulphur dioxide:

$$3SO_2+2K_2S_2O_3=2K_2S_3O_6+S.$$

The free acid is unstable; even at ordinary temperatures it decomposes in a dilute solution into sulphur, sulphurous oxide and sulphuric acid:

$$H_2S_3O_6=H_2SO_4+S+SO_2.$$

Tetrathionic acid. Its salts result from the action of iodine on the solution of a thiosulphate.

$$K_2S_2O_3+2I=2KI+K_2S_4O_6.$$

The acid itself can be obtained (also only in dilute solution) by adding sulphuric acid to the barium salt, which is prepared in an analogous manner. In dilute solution it is quite stable; in the concentrated state it breaks up into sulphur, sulphurous oxide and sulphuric acid.

Pentathionic acid. On mixing solutions of sulphur dioxide and hydrogen sulphide the principal reaction is a mutual oxidation and reduction of these compounds with the separation of sulphur (§ 78). The action is, however, much more complicated, inasmuch as polythionic acids, among them pentathionic acid, are formed in addition at the same time. The mixture of $H_2S.aq$ and $SO_2.aq$ is known as "WACKENRODER'S liquid." Well-crystallized salts of pentathionic acid have been prepared.

Use of Sodium Thiosulphate in Volumetric Analysis. Iodometry.

93. On adding sodium thiosulphate to an iodine solution, the intensely brown liquid loses its color, sodium iodide and sodium tetrathionate, two colorless compounds, being formed:

$$2Na_2S_2O_3+2I=Na_2S_4O_6+2NaI;$$

or, writing only the ions that take part in the reaction:

$$2S_2O_3''+2I=S_4O_6''+2I'.$$

The disappearance of the color is thus due to the fact that the molecules of iodine are transformed into ions by taking up two negative charges from $2S_2O_3''$. Upon this fact a method is based for determining the amount of free iodine in a solution. This is done by allowing a solution of sodium thiosulphate, whose concentration (*titre*) is known, to flow drop by drop into a definite volume of iodine solution. (For letting out a certain amount of liquid a **pipette** (Fig. 35) is commonly employed.) The color gradually brightens and finally a point is reached when the liquid is only slightly tinged and the addition of another drop causes the color to entirely disappear. This transition can be very accurately detected. The iodine molecules have now entirely disappeared. Since according to the above equation a molecule of thiosulphate is consumed for each atom of iodine, the percentage of iodine in the solution can be calculated from the amount of thiosulphate used.

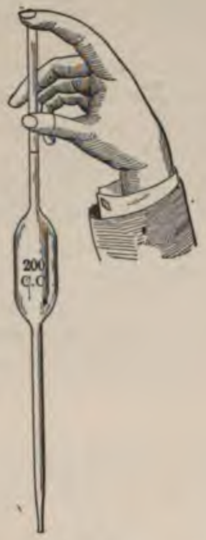


FIG. 35.—PIPETTE.

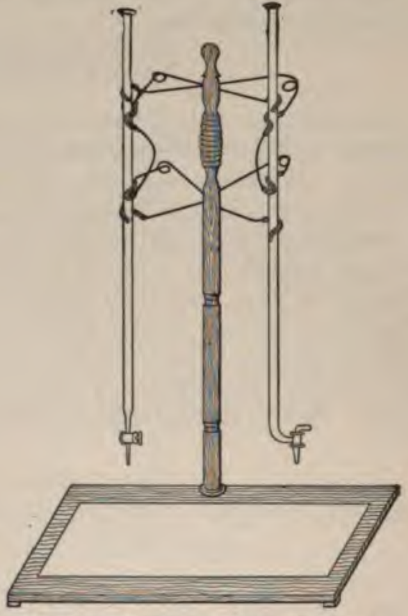


FIG. 36.—BURETTES AND SUPPORT.

To make the calculation of the result of such a determination (*titration*) as easy as possible the thiosulphate solution is so *stand* *ardized* that it bears a certain relation to an equivalent of iodine (=127 g.), i.e. a certain amount bleaches exactly this much iodine.

"**Normal solution**" is a name applied to a solution containing the equivalent weight (§ 23) in grams (*gram equivalent*) in one liter. Frequently use is also made of a ½, ¼, $\frac{1}{10}$ or a twice, thrice, etc., normal solution. Normal hydrochloric acid contains 36.5 g. HCl, normal sulphuric acid 49 g. H_2SO_4 (= ½ gram molecule), a normal iodine solution 127 g. iodine, per liter. Detailed directions for preparing such solutions can be found in the text-books of analytical chemistry.

In order to determine readily the volume of thiosulphate solution that is required in the analysis, use is made of a **burette** (Fig. 36), a glass tube that is divided into $\frac{1}{10}$ c.c. and closed at the lower end with a glass stop-cock or with a rubber tube and pinch-clamp. In titrating the iodine solution the thiosulphate solution is allowed to flow out slowly and, finally, drop by drop, while the liquid is being stirred.

Example. For 50 c.c. of an iodine solution whose strength is to be determined 27.30 c.c. $\frac{1}{10}$ normal thiosulphate solution was necessary before the color completely disappeared. Required the number of grams of iodine contained in 1 liter of this solution.

1000 c.c. $\frac{1}{10}$ normal $Na_2S_2O_3$ solution (see above) decolorizes $\frac{1}{10}$ equivalent of iodine (=12.7 g.); 27.3 c.c. therefore decolorizes $27.3\times\frac{12.7}{1000}$ g. iodine. This amount is contained in 50 c.c. of the iodine solution in question. Hence 1 liter of the latter contains $20\times27.3\times12.7\times10^{-3}=6.8842$ g. iodine.

Various other substances which liberate iodine from potassium iodide can be determined by titrating the amount of iodine displaced; for example, chlorine and bromine may be thus determined, since they set free the equivalent amount of iodine from potassium iodide solution.

SELENIUM AND TELLURIUM.

94. Selenium was discovered by BERZELIUS in 1817. It took its name from σελήνη (the moon), because it possesses great similarity to the element tellurium (named from *tellus* = the earth) discovered a short time previously. It is rather widely distributed in nature, but it occurs only in small quantities. It is found native, is frequently found in pyrite and also appears in some rare minerals. When this sort of pyrite is employed in sulphuric acid manufacture, the selenium collects in the "chamber-mud" of the lead chambers; from this it is usually obtained.

The process is as follows: The selenium deposit is heated with nitric acid, which oxidizes the selenium to selenic acid, H_2SeO_4. The solution thus obtained is first boiled with hydrochloric acid, whereby selenious acid, H_2SeO_3, is formed with the evolution of chlorine. This latter acid is then reduced by means of sulphurous oxide to selenium, which separates in amorphous red flakes.

Selenium displays analogy with sulphur in many respects; for instance, in occurring in various allotropic conditions. According to SAUNDERS, there is an amorphous red modification, that is soluble in carbon disulphide. From this solution the selenium separates as a second modification, which is the red crystalline selenium, fusing at 170°–180°. Then there is a metallic form fusing at 217°. This modification appears when amorphous selenium is heated to 97°, at which point a sudden and marked rise of temperature occurs; or when molten selenium is suddenly cooled to 210° and kept for a time at that temperature. In this metallic state selenium has a metallic lustre, is insoluble in carbon disulphide and conducts electricity. Its conductivity strangely depends very much on the intensity of its illumination, however.

The melting-point of selenium is 217°, its boiling-point 680°. As in the case of sulphur the vapor density decreases with rising temperature till about 1400° is reached, when it remains constant. At this temperature it is found to be 81.5 ($H=1$), corresponding to a molecular weight of 163.0. Now since the atomic weight of selenium, as deduced from the vapor density of its compounds, is 78.9, the above molecular weight agrees very closely with the formula Se_2.

Hydrogen selenide, H_2Se, can be obtained directly from its elements, as these unite at 400°. Analogously to hydrogen sulphide, it can also be got by the decomposition of iron selenide, $FeSe$, with hydrochloric acid. At a high temperature hydrogen selenide dissociates into its elements. Its properties are only slightly acidic and it is more poisonous than sulphuretted hydrogen. The heavy metals are precipitated from their solutions as selenides by it.

An aqueous hydrogen selenide solution becomes turbid on standing because of the selenium that separates out.

Two **chlorine compounds,** Se_2Cl_2 and $SeCl_4$, are known. The latter is much more stable than the corresponding sulphur compound, SCl_4 (§ 75). Selenium tetrachloride is solid and sublimes without decomposition; dissociation does not begin until 200° is reached.

Selenium dioxide, SeO_2, is the only oxide of selenium known. It results from the burning of selenium in the air. The extremely disagreeable odor which arises is not a property of the dioxide, however, but is probably due to the formation of another oxygen compound of selenium which has not as yet been isolated. Selenium dioxide forms long white needles that sublime at 310°.

Selenium dioxide is an acid anhydride; on dissolving it in water an acid, **selenious acid,** H_2SeO_3, is formed, which can be isolated (unlike sulphurous acid). This acid crystallizes in large colorless prisms. On being heated it breaks up into water and anhydride. Sulphur dioxide or stannous chloride reduce it to free selenium, which is deposited in red flakes:

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

Sulphuretted hydrogen precipitates from the solution selenium sulphide, SeS, insoluble in ammonium sulphide.

When chlorine is passed into the solution of selenious acid or when bromine is added to it, **selenic acid,** H_2SeO_4, is formed. In the pure state this is a crystalline solid, melting at 58°. The 95% solution of it is an oily liquid, which has the appearance of sulphuric acid. The barium salt of the acid, like that of sulphuric acid, is extremely difficultly soluble.

On boiling with hydrochloric acid, selenic acid is reduced to selenious acid with the evolution of chlorine.

Tellurium.

95. Tellurium is of rare occurrence; it is known in the native condition and also in combination with bismuth, and with gold or silver (in *sylvanite*, or *graphic tellurium*). It is found chiefly in Transylvania and in the Altai mountains, and also in Boulder Co., Colorado. In the amorphous condition tellurium is a black powder, but after fusion it is silvery

white, of a metallic lustre and a conductor of heat and electricity. The vapor density, as in the cases of selenium and sulphur, decreases with increasing temperature and does not remain constant till about 1400°; it then corresponds to a Te_2 molecule.

Hydrogen telluride, H_2Te, results from the action of hydrochloric acid on zinc telluride, $ZnTe$. The product thus obtained contains more or less hydrogen. It is very poisonous, and dissociates readily. From solutions of the heavy metals it precipitates their tellurium compounds (tellurides).

Tellurium dioxide, TeO_2, is formed on burning tellurium in the air. It is very difficultly soluble in water.

Tellurous acid, H_2TeO_3, is obtained by dissolving tellurium in nitric acid. It dissolves in water with great difficulty and breaks up on warming into TeO_2 and H_2O.

Telluric acid, H_2TeO_4, is prepared by fusing the metal or the dioxide with soda and saltpetre and separating the acid from the tellurate formed. The compound $H_2TeO_4 + 2H_2O$ crystallizes out from the aqueous solution; it loses its water of crystallization at 100°. The free telluric acid, H_2TeO_4, prepared in this way is a white powder, difficultly soluble in cold water. Telluric acid has only feebly acid properties.

Selenium and tellurium both combine with potassium cyanide, when they are fused with it, forming compounds corresponding to $KCNS$, viz., $KCNSe$ and $KCNTe$. Nevertheless, while potassium telluro-cyanide is at once decomposed by the oxygen of the air with the separation of tellurium, potassium selenio-cyanide is more stable and does not decompose with the separation of selenium until it is boiled with hydrochloric acid. We have here a means of detecting selenium in the presence of tellurium and of separating the two.

SUMMARY OF THE OXYGEN GROUP.

96. The elements oxygen, sulphur, selenium and tellurium, like the halogens, form a natural group, particularly in two respects; their compounds correspond to a general type and their physical and chemical properties vary gradually with increasing atomic weight. Their hydrogen compounds have the formula RH_2, their oxygen compounds and their acids the formulæ RO_2 and H_2RO_3, and also RO_3 and H_2RO_4. Ozone may be considered with reference to these types as analogous to sulphur dioxide; $O \cdot O_2$ ozone; $S \cdot O_2$ sulphur dioxide.

The following table shows the gradual change, or progression, of the physical properties:

	O.	S.	Se.	Te.
Atomic weight.....	16.00	32.06	79.2	127.6
Specific gravity....	1.124 (at −181°)	1.95–2.07	4.2–4.8	6.2
Melting-point......	....	114.5°	217°	452°
Boiling-point.......	−181.4°	450°	680°	white heat
Color..............	light blue	yellow	red	black

As the atomic weight increases, the values of the physical constants also increase, as the table shows. At the same time the external appearance approaches that of the metals; in tellurium the metallic appearance is quite marked.

The *instability of the hydrogen compounds* increases from oxygen to tellurium; the *strength of the oxygen acids* diminishes rapidly, sulphuric acid belonging to the strongest, and telluric acid to the very weak, acids.

It should also be noted that all of these elements appear in allotropic modifications.

THERMOCHEMISTRY.

97. It was stated above (§ 20) that a chemical combination or decomposition is accompanied by an evolution or absorption of heat, in other words by a heat change, or **caloric effect.** In many cases this caloric effect has been carefully measured. The work of BERTHELOT and of THOMSEN along this line has been especially fruitful. That part of chemistry which deals particularly with these caloric effects is called *thermochemistry.*

The caloric effect is always given for molecular amounts of the reacting substances, since in this way only is it possible to compare substances from a chemical standpoint. Hence, when the **heat of formation** of water is said to be 69.0 calories (kilogram calories), it is implied that this number of calories is evolved by the union of 2 g. hydrogen with 16 g. oxygen:

$$2H + O = H_2O + 69.0\,\text{Cal.}$$

In this equation H and O stand for gram atoms.

In expressing a caloric effect it is necessary to indicate the state of matter of the reacting and the resulting substances, in so far as this is not self-evident, because the latent heat of fusion or vaporization must be taken into consideration. The above amount,

$$2H+O-H_2O_{liquid}=69.0 \text{ Cal.},$$

refers to the formation of water and its conversion to a liquid. It therefore includes the heat of condensation. Since this amounts to 0.536 Cal. per gram, it would in this case (for 18 g.) be 9.6 Cal.; hence the caloric effect of the combustion of hydrogen to steam at 100° is

$$2H+O=H_2O_{gas}+58.4 \text{ Cal.}$$

The caloric effect is also influenced by the condition, whether solid or dissolved, in which the substances react, inasmuch as solution is almost always accompanied by a heat change. In the formation of sodium chloride by the mixture of dilute solutions of sodium hydroxide and hydrochloric acid (this being indicated by aq after the formulæ of the substances) the caloric effect is:

$$NaOH_{aq}+HCl_{aq}=NaCl_{aq}+H_2O+13.7 \text{ Cal.}$$

However, when the salt is prepared by passing hydrochloric acid gas into a dilute solution of the base, the equation is as follows:

$$NaOH_{aq}+HCl_{gas}=NaCl_{aq}+H_2O+31.1 \text{ Cal.}$$

We thus obtain 13.7 Cal. as before, but increased by the heat of solution of gaseous hydrochloric acid in a large amount of water, viz., 17.4 Cal.

The heat of formation of chemical compounds must be equal to their heat of decomposition, but have the opposite sign. Were this not the case, heat would be lost or gained when a compound is formed and then decomposed so as to return to the original condition, and such a result would be at variance with the Law of the Conservation of Energy.

In many instances a distinction must be made between *heat changes* and *energy changes* in a reaction, particularly wherever positive or negative work is done on the system from without. For example, work is performed by the surroundings when the reaction takes place under atmospheric pressure, and is attended by a decrease of volume. In this instance the heat evolved, Q, represents the sum of the energy produced, E, and the work, W, performed from without. $Q = E + W$. In the case of reactions attended by an increase of volume under constant pressure W is negative, hence $Q = E - W$.

The difference between the evolution of heat and of energy in such cases is not always to be overlooked, especially when the change of volume is a result of the increase or diminution of the number of gas molecules. In that case the difference is considerable, but is easily calculated. The evolution of heat amounts to $2T$ g.-cal. (§ 34), i.e., at ordinary temperatures about 0.6 Cal. more than the energy given off for each gram-molecule of gas that disappears in the reaction (over and above any new gas produced).

Energy generated, $2H + O - H_2O_{liquid} = 69.0$ Cal.
Heat generated, $2H + O - H_2O_{liquid} = 69.9$ Cal.

The difference, +0.9 Cal., is due to the disappearance of 1½ gram-molecules of gas.

Experience has shown that in the formation of most compounds heat is generated, but that in many cases heat is absorbed. Chemical actions of the first sort are called **exothermic**, those of the second **endothermic**, reactions. An example of the second sort is the synthesis of chlorine monoxide:

$$2Cl + O = Cl_2O_{gas} - 15.1 \text{ Cal.}$$

98. For the **determination of the caloric effect** various methods are in use. Only those actions are suitable for thermochemical measurements which complete themselves quickly. In measuring the caloric effect in the case of liquids or solutions, as, for example, the **heat of neutralization** of acids and bases, the **heat of solution** or of **dilution**, etc., an ordinary calorimeter is generally used, such as is employed in physics for the method of mixtures, the same precautions being taken in order to secure accurate results.

The **heat of combustion** of a substance is usually measured with the *calorimetric bomb* of BERTHELOT-MAHLER. This is the usual method with organic compounds.

99. **The Law of HESS.** *The entire caloric effect (the whole amount of energy) produced by the transformation of one chemical system into another is independent of all intermediate stages.*

This law is a direct consequence of the principle of the conservation of energy. If Hess's law did not hold, energy would have to be gained or lost in the transition from one system to another and the subsequent return to the initial condition, which is contradictory to the above principle. A few examples will serve to make this law more clearly understood.

(*a*) A dilute solution of sodium sulphate can be prepared from sodium hydroxide, sulphuric acid and water in various ways. For instance, two gram-molecules of the base can be treated at once with dilute sulphuric acid; or one gram-molecule of the base can be mixed with the acid at first and the second added afterward. Accordingly we get the following caloric effects:

$$\begin{array}{llr} (1) & 2NaOH + H_2SO_{4aq} - Na_2SO_{4aq} - 2H_2O = & 31.4 \text{ Cal.} \\ (2) & \left\{\begin{array}{l} NaOH_{aq} + H_2SO_{4aq} - NaHSO_{4aq} - H_2O = 14.75 \\ NaOH_{aq} + NaHSO_{4aq} - Na_2SO_{4aq} - H_2O = 16.65 \end{array}\right. & \\ & \text{Total} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & 31.4 \text{ Cal.} \end{array}$$

(*b*) From ammonia, hydrogen chloride and water a dilute solution of ammonium chloride, NH_4Cl, can be prepared, either by letting dry ammonia gas combine with dry hydrogen chloride gas and dissolving the resulting ammonium chloride in water or by first dissolving ammonia and hydrogen chloride in separate portions of water and then mixing the solutions. In the first case we have the equations:

$$\begin{array}{lr} NH_{3gas} + HCl_{gas} - NH_4Cl_{solid} \ldots\ldots\ldots\ldots = & 42.6 \\ NH_4Cl_{solid} + aq - NH_4Cl_{aq} \ldots\ldots\ldots\ldots\ldots = & -\ 4.0 \\ \hline & 38.6 \text{ Cal.} \end{array}$$

in the second case:

$$\begin{array}{lr} NH_3 + aq - NH_{3aq} \ldots\ldots\ldots\ldots\ldots\ldots = & 8.82 \\ HCl + aq - HCl_{aq} \ldots\ldots\ldots\ldots\ldots\ldots = & 17.13 \\ NH_{3aq} + HCl_{aq} - NH_4Cl_{aq} \ldots\ldots\ldots = & 12.45 \\ \hline & 38.40 \text{ Cal.} \end{array}$$

The final effects in the two cases are found to be alike within the limits of experimental error.

With the help of Hess's law the determination of the caloric effect is rendered possible in many reactions which cannot be dealt with directly or are unsuitable for calorimetric measurements. In general this is done by making thermochemical measurements for a series of processes in which the reaction plays a part and finally calculating the caloric effect of the reaction as the single unknown, as will be more fully explained in the examples below.

Suppose it were required to find the heat of formation of hydrogen sulphide. This compound can be formed directly from its elements (§ 72), but only in a way unsuitable for thermochemical study. We will then start with the system, H, S, and O, and conceive it as undergoing the following changes: (1) hydrogen and sulphur are burned to water and sulphur dioxide; (2) hydrogen and sulphur are combined and the hydrogen sulphide formed is burned to water and sulphur dioxide. Since we started with the same system and in the end reached the same result in each case, the caloric effect must be the same according to Hess's law. We therefore have:

Heat of combustion of H + heat of combustion of S = heat of formation of H_2S + heat of combustion of H_2S.

$$(2H + O - H_2O) + (S + 2O - SO_2) =$$
$$(2H + S - H_2S) + (H_2S + 3O - SO_2 - H_2O).$$
$$68.0 + 69.26 = x + 133.46;$$
$$\therefore \quad x = (S + 2H - H_2S) = 3.8.$$

It is a somewhat more complicated task to determine the heat of formation of hypochlorous acid, an example of a compound that cannot be prepared directly from its elements. It is computed in the following way: When a solution of this acid is mixed with hydriodic acid, it decomposes according to the following equation:

$$HOCl_{aq} + 2HI_{aq} = 2I + HCl_{aq} + H_2O + 50.41 \text{ Cal.}$$

This amount of heat evolved is the algebraic sum of the following caloric effects: (1) decomposition of $HOCl_{aq}$, unknown; (2) decomposition of $2HI_{aq} = -26.34$; (3) formation of $HCl_{aq} = 39.4$; (4) formation of water $= 68.0$.

The equation thus becomes

$$-x-26.34+39.4+68.0=50.41;$$

and

$$x=+30.65 \text{ Cal.}$$

100. In using these values of the heat of formation and heat of decomposition it should be noted that they do not represent the amounts of heat liberated by the combination of atoms to form molecules, but that the heat of decomposition of the molecules of the elements (i.e. the amount of heat required to break these molecules up into atoms) is always included. When, for example, chlorine unites with hydrogen to form hydrochloric acid, 22.0 Cal. are given off. That which is measured is the **total caloric difference** between the initial system H_2+Cl_2 and the 2HCl formed from it. In the indirect determination of a heat of formation with the help of HESS's law the calculated caloric effect also includes the heat of decomposition of the molecules of the elements. In the determination of the heat of formation of hydrogen sulphide, for instance, in the above way the caloric effect of the combustion of this gas is composed of the following parts:

$$2(2H+S-H_2S)+3(2O-O_2)=2SO_2+2H_2O+p \text{ Cal.};$$

that of the combustion of hydrogen of the following:

$$2(2H-H_2)+(2O-O_2)=2H_2O+q \text{ Cal.};$$

that of the combustion of sulphur of

$$(2S-S_2)+2(2O-O_2)=2SO_2+r \text{ Cal.};$$

$(2O-O_2)$, etc., indicating the heat of decomposition of molecules of the elements.

The heat of formation of hydrogen sulphide is $r+q-p$. Deducing the value of $r+q-p$ from the above equations, we have

$$r+q-p=(2S-S_2)+2(2H-H_2)-2(2H+S-H_2S),$$

from which it follows that the heats of formation of the sulphur and hydrogen molecules are included in the heat of formation found.

101. Experience has shown that ordinarily those chemical processes take place whose effects are exothermic, while those which would have an endothermic effect do not take place. This affords us a useful means of often foretelling the direction of a reaction. The formation of water or hydrogen chloride is accompanied by the evolution of considerable heat; that of chlorine monoxide, Cl_2O, on the contrary, is endothermic; as a matter of fact the latter substance cannot be obtained directly from its constituent elements, while this is possible with water and hydrochloric acid. Iodine is displaced from metal iodides by chlorine, chlorides and free iodide being formed. The equation is

$$KI + Cl = KCl + I + 25.5 \text{ Cal.}$$

On the other hand, iodine cannot liberate chlorine from potassium chloride, since this action would consume 25.5 Cal. Many examples could be given of reactions which might proceed in various directions, but take that one which involves an evolution of heat.

It might therefore be supposed that the heat given off in a reaction could be regarded as a measure of the affinity satisfied by it; but reasons, furnished by thermodynamics, prove that this cannot be correct. The application of the methods of thermodynamics to chemical problems has led to clear views concerning this and many other kindred matters. One of the most important deductions of thermodynamics is the phase rule (§ 71), which has already been applied in numerous instances. Another is LE CHATELIER'S rule, which we shall next consider.

LE CHATELIER'S RULE.

102. *When any system is in physical or chemical equilibrium, a change in one of its equilibrium factors produces a change in the system, whose effect is opposite to that of the former change.*

This rule, or theorem, which can be called the **principle of the resistance of the reaction to the action,** furnishes us with a convenient means of foretelling in many instances the direction which a reaction will follow. Some examples may be given to illustrate the rule.

(1) When a system of water and ice is subjected to increased pressure, the ice melts; that is, that process goes on which involves

a contraction, for by this contraction the system diminishes the pressure exerted on it.

(2) Monoclinic sulphur, when compressed near the transition point (the temperature of equilibrium for ordinary pressure), passes over into rhombic sulphur, since this process involves a lessening of volume, and in the end also a diminution of pressure, as in the previous case.

(3) When a solution is diluted the osmotic pressure decreases according to BOYLE's law; in the case of a solution of an electrolyte dilution will be followed by farther dissociation, since this increases the osmotic pressure.

(4) When a liquid is heated, more vapor is formed; since the vaporization absorbs heat, its effect is opposite to that of the heating.

103. VAN'T HOFF's **principle of mobile equilibrium** is an application of this rule to a special case. It says: *An equilibrium between two different states of matter (systems) displaces itself under constant pressure by a* $\frac{\textit{fall}}{\textit{rise}}$ *of temperature to that one of the two systems whose formation* $\frac{\textit{evolves}}{\textit{absorbs}}$ *heat.* A few examples will serve to make this clear.

(1) Rhombic sulphur becomes monoclinic when heated above the transition point, since heat is absorbed by this transition. Below this temperature the inverse transition takes place. (Ordinary pressure is assumed in each case.) The reaction works in opposition to the temperature change produced from without.

(2) A salt whose heat of solution is negative (saltpetre) dissolves to a greater degree if the temperature rises. If its heat of solution is positive, a rise of temperature causes a separation from solution (§ 235). This principle leads to a further very remarkable deduction. Since an elevation of the temperature requires the displacement of the equilibrium in the direction of that system which is formed with absorption of heat, endothermic reactions must predominate at high temperatures. On the other hand, exothermic reactions must be generally associated with low temperatures. From the mathematical form of the principle it follows that at the absolute zero all reactions must be exothermic. At the prevailing room temperature, which is not so very far—approximately 300°—above the absolute zero,

most reactions are still exothermic, although endothermic reactions do occur (formation of Cl_2O, etc.). At the temperature of the electric arc (2000–2500°) exothermic compounds are mostly incapable of existence, endothermic compounds being obtained. We saw above, that ozone and hydrogen peroxide, both endothermic, are formed at a very high temperature (§§ 36 and 38); and we shall later see that the endothermic compounds nitric oxide (§§ 120 and 127) and acetylene (§ 180) can be synthesized in the heat of the electric arc.

104. There is still another deduction from thermodynamics worthy of notice here. Thermodynamics furnishes us in a very general way with a means of determining whether or not a reaction is possible. Nevertheless it does not require that the particular reaction which is possible should really take place. The thought then suggests itself at once that, where reactions which are possible do not take place, there are conditions existing which were overlooked in the application of the thermodynamical laws and which prevent the reaction from occurring. Such conditions, of which there are indeed indications in many cases, may be comprehensively termed **passive resistances.** They may be capillary actions, perhaps, or mechanical hindrances or friction or something of that sort. These passive resistances may sometimes greatly retard the reaction velocity, especially at low temperatures. We already saw an example of this in § 12 in a mixture of hydrogen and oxygen. Moreover PICTET has shown that sodium, which reacts rather vigorously with alcohol at ordinary temperatures, floats on it quietly at − 80° without any apparent reaction; even concentrated hydrochloric acid and marble do not react upon each other, or at least only very slowly, when they are cooled to a low temperature.

It has been found from thermodynamical laws that the variation of the reaction velocity with the temperature may in general be expressed thus: when the temperature increases arithmetically, the velocity increases geometrically. Experience has farther shown that a temperature rise of ten degrees generally involves about a doubling or trebling of the reaction velocity.

It is not difficult to see what an exceedingly important rôle the passive resistances above referred to play in nature. Were it not for them, the phenomenon of combustion, the oxidation of metals, etc., could take place at ordinary temperatures; everything combustible would then burn and there could be no animal and vegetable life on the earth.

NITROGEN.

105. This element occurs free in the air, which contains about 80% nitrogen and 20% oxygen. In combination, it is found in the salts of nitric acid, e.g. saltpetre, and also in the albuminoids, which form an important constitutent of animal and vegetable organisms.

Nitrogen can be easily isolated from the air by removing the oxygen. This is accomplished in various ways. Phosphorus, when burned in the air, absorbs the oxygen to form phosphorus pentoxide, and the residual gas, aside from slight admixtures (§ 110), is nitrogen. Again, air can be passed over heated copper in a finely divided condition, whereupon copper oxide is formed and nitrogen left.

In this process the oxygen of the air soon converts all the copper into copper oxide, so that of course only a limited amount of nitrogen can thus be obtained with the aid of a given amount of copper. However, if the air is first passed through ammonia water, the process can be carried on continuously, since the hydrogen of the ammonia, NH_3, constantly reduces the oxidized copper.

Copper can also absorb the oxygen of the air at ordinary temperatures, if it is treated with a solution of ammonia and ammonium carbonate. Moist phosphorus combines with oxygen even at ordinary temperatures, so that a volume of air which remains in contact with pieces of phosphorus for some minutes loses its oxygen. An alkaline solution of pyrogallol also has the ability to absorb oxygen at ordinary temperatures. These reactions are made use of in gas analysis.

106. Pure nitrogen is obtained by the direct decomposition of certain of its compounds, especially by heating ammonium nitrite.

$$NH_4NO_2 = N_2 + 2H_2O.$$

This is usually accomplished by boiling a solution of equal parts by weight of potassium nitrite, KNO_2, sal ammoniac, NH_4Cl, and potassium dichromate, $K_2Cr_2O_7$, in 3 parts of water. The NH_4Cl and KNO_2 react to form KCl and NH_4NO_2.

By heating ammonium chromate, $(NH_4)_2CrO_4$ (a mixture of ammonium chloride and potassium dichromate is more convenient), nitrogen is also set free:

$$K_2Cr_2O_7+2NH_4Cl=N_2+Cr_2O_3+2KCl+4H_2O.$$

An example of the formation of nitrogen by the indirect decomposition of its compounds is the reduction of nitrogen oxides by hot copper:

$$2NO+2Cu=N_2+2CuO.$$

Physical Properties.—Nitrogen is a colorless and tasteless gas. Its specific gravity based on air is 0.9682, its density compared with hydrogen is therefore 13.93. 1 l. N weighs 1.2521 g. at 0° and 760 mm. It is one of the most difficult gases to condense, its critical temperature being −146°. Its boiling-point is −194°. At −214° it becomes solid. It is only slightly soluble in water, even less so than oxygen.

Chemical Properties.—Nitrogen is chemically very indifferent; it unites with no element at ordinary temperatures and at higher temperatures with only a few. Boron, silicon, titanium, barium, strontium, calcium, magnesium, chromium and also certain rare elements combine directly with nitrogen at red heat, forming nitrides. Magnesium nitride has the formula Mg_3N_2. Nitrogen unites with oxygen under the influence of induction sparks directly (reddish brown NO_2 being formed); with hydrogen it combines in a similar way. When a mixture of hydrogen and nitrogen, together with a few drops of concentrated hydrochloric acid, is introduced into a tube over mercury and induction sparks are sent through, clouds of ammonium chloride, NH_4Cl, are produced, the nitrogen and hydrogen having united to form ammonia, NH_3. These last two reactions and the fact that nitrogen is not able to support combustion serve for the identification of nitrogen gas.

The *molecule of nitrogen* consists of two atoms, this having been demonstrated in the same way as for oxygen and other gaseous elements.

THE ATMOSPHERE.

107. The air was regarded as an element up to the end of the eighteenth century. It finally developed from the investigations of PRIESTLEY and LAVOISIER that it is not a simple body. The correct explanation of the phenomena of combustion led to this conclusion.

Before LAVOISIER'S time the explanation of the phenomena of combustion was just the reverse of the present one. It was then thought that all combustible or oxidizable substances had a common constituent, **phlogiston.** According to this theory, which was presented by STAHL (1660–1734), the combustion of a body is due to the escape of phlogiston. If this occurs in a violent manner we have the phenomenon of fire. The more inflammable a substance is, the more phlogiston it was supposed to contain. Sulphur, phosphorus, carbon and hydrogen therefore ranked as being very rich in phlogiston. As to the real nature of this phlogiston opinions were decidedly different. At various times experiments were performed with the hope of isolating the substance. For a while it was thought with CAVENDISH that hydrogen was pure phlogiston.

The prevailing ideas were as follows: Substances that possess much phlogiston can transfer it to those which have none or very little. The metals, for example, are substances that contain a certain amount of phlogiston, which they give off on being heated in the air; by this process they are changed to calxes (now called oxides), which contain no phlogiston. When one of these calxes is heated with carbon or hydrogen, it absorbs phlogiston from them and is changed back again to the metal. The fact that sulphur, phosphorus or any other inflammable substance soon ceases to burn when it is enclosed in an air-tight space was explained by the supposition that the air has then become so saturated with phlogiston that the latter can no longer escape from the burning body.

We see from the above that this theory led men to view many phenomena from a common standpoint and undoubtedly contributed in no small degree to the advancement of chemistry. So long as the phenomena of burning were regarded in that light, there was no occasion to doubt the elemental nature of air. They believed that bodies lose something when they are burned, while we now know that on the contrary something is taken up from the air. The great mistake of the phlogiston theory was, that it did not regard the increase in weight of the burned body; as soon as LAVOISIER and others drew attention to this most important fact, the phlogiston theory could no longer be upheld.

On the first of August, 1774, PRIESTLEY had discovered oxygen, which he himself regarded as air devoid of phlogiston ("dephlogisticated air");* **Lavoisier**, however, recognized this substance as the essential principle of all burning and oxidation. It now required only a step to reach the conception that air is not an element, but contains another gas in addition to oxygen, and that this gas does not support combustion. The experiment by which **Lavoisier** demonstrated this has been already described (§ 9). By measuring the amount of nitrogen which remained after the absorption of the oxygen by hot mercury he was able to determine fairly accurately the composition of air.

108. *Constituents of the Atmosphere.*—Besides oxygen and nitrogen air contains argon and the other elements described in § 110, hydrogen (0.02%), and also variable amounts of water vapor, carbon dioxide (very nearly 0.04% on the average), ammonia, ozone, and perhaps hydrogen peroxide (the last three in extremely small quantities). Incidentally sulphur dioxide and other gases are found in the air (e.g. in the vicinity of volcanoes). The lower strata of air always contain floating dust particles, microbes, etc.

Analysis of Air.—The proportional amounts of oxygen and nitrogen in carefully dried air, free from carbon dioxide, etc., has been repeatedly determined with all due precaution. According to the method of **Dumas** and **Boussingault** this can be done as follows:

The tube, *ab* (Fig. 37), containing copper turnings is connected with the globe, *V*, all air having been removed from both. The end of the tube marked *b* is attached to the various pieces of apparatus *C*, *B* and *A*, which are to remove the carbon dioxide and water vapor from the inflowing air. The globe, *V*, is first carefully weighed without air. Thereupon the tube is heated by means of a furnace and a slow current of air is allowed to pass through it to the globe by partially opening the stop-cocks *u* and *r*, the oxygen being meanwhile asborbed by the hot copper. By subsequently weighing the globe the amount of nitrogen which it contains can be determined and by weighing the tube before and after we can find the amount of oxygen. In this way the ratio of oxygen to nitrogen in air can be ascertained.

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* From the letters and laboratory notes of **Scheele**, published by Baron **Nordenskiöld** (Stockholm, 1892), it is evident that oxygen was known to **Scheele** sooner than to **Priestley**; he called it "*Feuerluft.*" However, this discovery did not seem to lead him any nearer than **Priestley** to a correct understanding of the phenomena of burning.

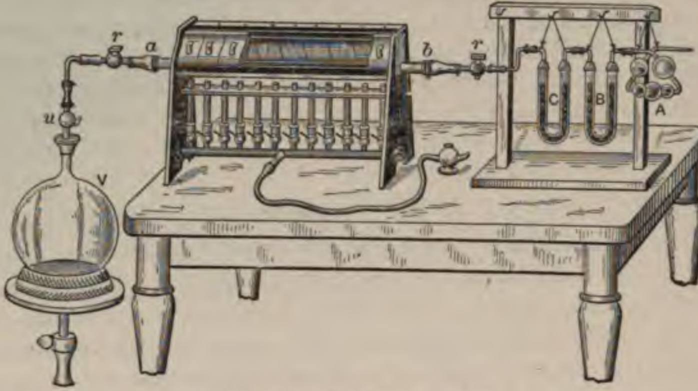


FIG. 37.—ANALYSIS OF AIR.

Another method is the *eudiometric method*. A known volume of air is mixed with a sufficient known volume of pure (electrolytic) hydrogen. On allowing an electric spark to pass through, the hydrogen and oxygen unite to form water, which is deposited on the sides of the vessel. Inasmuch as 2 vols. hydrogen combine with 1 vol. oxygen, one-third of the volume that disappeared must have been oxygen.

109. These and other methods of investigation have shown that *the composition of the air is nearly constant.* In all parts of the earth, as well as at the highest altitudes which balloons have reached, it consists of

20.81% oxygen and 79.19% nitrogen by volume; and
23.01% " " 76.99% " " weight.

The observed variations from this ratio amount to hardly ±0.1%. Moreover, the composition does not appear to change with time; our present analyses agree with those of DUMAS and BOUSSINGAULT made in 1841.

This result seems surprising at first thought, because oxygen and nitrogen are constantly being removed from the air and again returned to it and it does not necessarily follow, indeed it is rather an improbability, that the losses and gains will exactly balance.

The oxygen passes through the following cycle: Free oxygen is consumed in all sorts of oxidations of which the *mineralization* of organic matter is the most important. By the term "mineralization" is meant the oxidation of the residues of plants and animals by the oxygen of the air with the aid of bacilli. The carbon of these residues is oxidized to carbon dioxide; the nitrogen, phosphorus, sulphur and other elements return to the "mineral" state, as nitrates, sulphates, etc. Along with this process there are the other oxygen-consuming processes of the respiration of animals and plants and the burning of fuels, carbon dioxide being formed in all cases. This carbon dioxide is employed by the plants in their process of assimilation, the oxygen in it being again given back to the air. It will therefore depend on the relative magnitude of this process as to whether just as much oxygen gets back into the air as was previously taken up in the formation of carbon dioxide. The oxygen which serves for other oxidations does not necessarily return to the air.

Nitrogen passes through a cycle too. Most of the nitrogen that occurs in the form of organic compounds in animal and vegetable tissues remains in the combined state after the death of the organism, either as ammonia or as nitric acid or in other nitrogenous products. During the process of decay the combined nitrogen is partially liberated; in the burning of plant and animal remains all of it is set free. On the other hand, certain plants, the *Leguminosæ*, are able by symbiosis with bacteria to absorb free nitrogen from the air directly. There are also bacteria which, acting alone, can assimilate nitrogen. Moreover, in storms some nitrogen combines with oxygen, and again, silent electric discharges, such as must frequently pass between earth and clouds, cause the nitrogen to enter into combination. Here the question again arises whether as much comes back to the air as goes out.

From what has been said it is sufficiently clear that it would be a mere coincidence if exactly as much oxygen should happen to be withdrawn as is given back. Approximate compensation probably takes place, but, even if it should not, the atmosphere is so vast that its composition would be only slightly affected in the course of centuries.

The following calculation will convince one of the soundness of this argument: The normal atmospheric pressure is 760 mm. mercury; this is due to the weight of the air and the moisture in it. Granted that the pressure of the latter averages 10 mm., we have 750 mm. left for the pressure of the air itself; i.e. the weight of the air is equal to that of a layer of mercury 750 mm. thick extending over the entire surface of the earth. This weight can be calculated thus: The volume of the space between two concentric spheres is $4\pi R^2r$, if R is the radius of the inner sphere, and r the thickness of that space. The radius of the earth (R) is, on the average, 6,370,284 m.; r is 0.75 m.; therefore, taking into consideration the specific gravity of mercury (13.59), we have for the desired weight of mercury or air 5.2×10^{18} kilograms. Since 1 m.^{3} air at 0° and 760 mm. pressure weighs 1.2932 kg., the above weight corresponds to a volume of air of 4×10^{18} m.^{3} (at 0° and 760 mm.) or $\frac{1}{5}\times10^{18}=8\times10^{17}$ m.^{3} of oxygen. In comparison with this the amount of oxygen which is withdrawn from the air in breathing, burning, etc., is very small. An adult human being consumes about 600 liters of oxygen every twenty-four hours, or 219,000 liters (219 m.^{3}) a year. The population of the earth is not quite 1500×10^6; all these people therefore require 328.5×10^9 m.^{3} of oxygen in a year. Assuming farther, which is a very high estimate, that the total consumption of oxygen is ten times the amount required for human respiration, the atmosphere would be deprived each year of 328.5×10^{10} m.^{3}, i.e. the 416×10^{-6}th part of the whole amount. The relative insignificance of this amount is better understood when we reflect that 0.1% of all the oxygen on hand would be 8×10^{14} m.^{3}. According to the above calculation of the annual need there would be enough oxygen to supply the demand for 244 years without allowing for any compensation. Since, however, the assimilative process of the plants yields a considerable amount in addition, the variations in the proportion of oxygen in the air must obviously be imperceptible with our present analytical methods.

The air is a mixture. It cannot be a compound of nitrogen and oxygen for the following reasons: (1) the ratio of nitrogen to oxygen is different than it would be for a compound of the two elements, for in the latter case it would have to correspond to the ratio of the atomic weights or a multiple of the same; (2) by mixing nitrogen and oxygen in the ratio in which they exist in air a synthetical air is obtained which is in every respect like that around us. (This excludes the possibility of air containing a perceptible amount of a compound of the two elements in addition to free nitrogen and free oxygen.) (3) The ratio of the solubilities of the oxygen and the nitrogen of the air in liquids is the same as that calculated from the solubilities of the pure gases oxygen and nitrogen, after taking into account their partial pressures. This could not be the case if the air contained a compound of oxygen and nitrogen; (4) when liquid air boils the first part of the distillate is chiefly nitrogen.

The *liquefaction of air* is now carried on in commerce. The methods used by LINDE and by HAMPSON are based on the same principle, namely, cooling the air by expansion. Further details may be found in text-books on physics.

Liquid air is very mobile and has a bluish tint. It is usually somewhat cloudy because of suspended particles of ice (congealed atmospheric moisture) and solid carbon dioxide. These may be removed by filtration through filter-paper. It boils at about −190°. It is now extensively used in producing, and demonstrating the effects of, very low temperatures. When carbon dioxide, for example, is led into a flask containing liquid air, it falls in the solid form like snow-flakes. In spite of its low temperature liquid air can be poured upon the hand without danger; it does not even feel cold (on account of the LEYDENFROST phenomenon). Liquid air is much richer in oxygen than the gaseous air of the atmosphere, containing about 50%. If a glowing splinter is dipped into the liquid, the wood begins to burn very vigorously, producing a violent reaction. It can be preserved for a rather long time in vacuum flasks.

ARGON, HELIUM AND COMPANION ELEMENTS.

110. Argon. Despite the fact that air had been already analyzed times without number, it was first discovered in the course of investigations by RAYLEIGH and RAMSAY in 1894 that there are other elements in the air than nitrogen and oxygen. One of these, named *argon* by its discoverers, is even found to the extent of 0.9% by volume, or 1.2% by weight. It was on account of its extraordinary resemblance to nitrogen that it was so long overlooked. The first indication of its presence was the observation that the specific gravity of the nitrogen isolated from the air is somewhat higher than that of the nitrogen prepared from ammonium nitrite and other compounds. 1 liter of nitrogen from air weighed 1.2572 g., while the same amount from chemical compounds weighed 1.2521 g., in both cases at 0° and

760 mm. There must therefore be another gas heavier than nitrogen, mixed in with the nitrogen of the air.

Two methods were employed by the investigators above named to isolate this gas. The first one was to pass the air over hot copper in order to remove the oxygen, and then over red-hot magnesium, which absorbs the nitrogen (§ 107). There still remained a small quantity of gas which was not nitrogen. The other method was to subject a mixture of air and oxygen over caustic potash to the action of induction sparks for a long time. The oxygen unites with the nitrogen, forming compounds which are absorbed by the potash. At the end the excess of oxygen is removed by some absorbing-agent (§ 105). In this case also there is a remainder of gas. Still other methods have been devised for obtaining argon from the air. One of the simplest is to heat air with a mixture of 1 g. magnesium, 0.25 g. sodium and 5 gr. freshly ignited lime. On account of the high temperature free calcium is formed:

$$Mg + CaO = MgO + Ca,$$

and it is in such a finely divided condition that it absorbs oxygen greedily and also nitrogen, so that only argon is left.

After argon had been once discovered it was found elsewhere than in the atmosphere; some mineral waters contain it in solution, certain rare minerals yield it when heated, etc.

Argon is a colorless, odorless gas, having a vapor density of 19.957. It has been condensed to a colorless liquid, that boils at -186.9°, by cooling with boiling oxygen and compressing to about 50.6 atmospheres; it solidifies at -189.6°. It is somewhat more soluble in water than is nitrogen (0.05780 parts in 1 vol. at 0° and 760 mm. pressure). As to its chemical nature, it is interesting that no one has yet succeeded in preparing a compound of argon.

It is certain that what is now called argon is neither a mixture nor a compound, but an element. The boiling-point and the melting-point are constant, and the vapor pressure of argon likewise remains constant during the liquefaction, so long as any gas is present. Moreover, when a certain volume of argon is three-fourths dissolved in water, the undissolved gas shows exactly the same spectrum as the dissolved. All of the above are characteristics of a homogeneous substance. The extraordinary stability of the gas in the presence of all sorts of reagents is a strong argument against its being a compound.

111. After the discovery of argon Ramsay and Travers detected four other rare gases in the atmosphere, though their quantity is very small. These are *helium*, *neon*, *krypton*, and *xenon*. In a spectroscopic investigation (§ 266) Norman Lockyer had detected in the atmospheres of the sun and many fixed stars considerable quantities of a gas unknown on the earth; he named it *helium*. In 1895 Ramsay and Travers succeeded, however, in obtaining it in small amounts on heating the rare mineral *cleveite*. Afterward it was also met with as a companion of argon in certain other, chiefly uraniferous, minerals as well as in mineral springs, for instance those of Bath. When air is liquefied, a part of it always escapes condensation; this part consists chiefly of nitrogen, but contains also helium and neon. Nitrogen can be removed from this mixture by the methods already described above (p. 165). When the resulting mixture of helium and neon is then cooled with boiling hydrogen, neon alone is condensed.

At ordinary temperatures helium is a colorless gas; very recently Kamerlingh Onnes succeeded in solidifying it by cooling with solid hydrogen and expanding at the same time. The critical temperature is about +3° abs. It is less soluble in water than argon.

Dewar proved that helium and neon can be isolated directly from the air by bringing the air in contact with ignited charcoal at −185°. The charcoal has the curious property of condensing in its pores all the other gases of the air, and a gaseous residue is here obtained which shows clearly the spectral lines of He and Ne.

While helium and neon were found in the most volatile part of the air krypton and xenon were obtained, on the contrary, from the residue, after a large quantity of liquid air had been allowed to evaporate slowly. Their separation was rendered possible by the fact that krypton still has a rather large vapor tension at the temperature of liquid air, while the vapor tension of xenon is then imperceptible.

Both these elements occur only in extremely small amounts in the atmosphere. In a recent investigation Ramsay found one part of krypton in seven million parts of air and one part of xenon in forty million parts of air (both by weight.) Of helium one vol. is present in 245,300 vols. of air.

In the following table some of the data of these elements are given. The elements form a natural group.

	Helium.	Neon.	Argon.	Krypton.	Xenon.
Density (O=16)..	1 98	9.97	19.96	40.88	64
Atomic weight.....	4	20	39.9	81.8	128
Boiling - point at 760 mm........	....	....	86.9° abs.	121.9° abs.	163.9° abs.

These gases have three properties in common which are worthy of mention here. In the first place they display characteristic spectral lines in Plücker tubes (§ 263), whereby it has been possible to recognize them and to judge of their purity. In the second place, no one of these elements has been found to enter into combination with other elements; they may therefore be considered nullivalent. In the third place, their molecule consists of only one atom. This fact could not be discovered in the ordinary way, described in §§ 33 and 34, because of the entire absence of compounds for investigation. It has, however, been possible to ascertain it from the *molecular heat* of the gases. This is the amount of heat that must be imparted to a gram molecule of a gas in order to raise its temperature one degree. This quantity of heat differs, according as the gas is under constant pressure or under constant volume. It is greater in the first case because under constant pressure the gas expands on heating and so does work, which evidently involves an expenditure of heat. We saw in § 35 that for one gram molecule of a gas the equation $PV=2T$ is applicable, the $2T$ expressing in calories the external work done when a gas under constant pressure P increases its volume by V, or when a gas being generated under the pressure P comes to occupy a volume V. If the temperature is raised one degree we have $PV=2(T+1)$; for each gram molecule of gas extra work is therefore done equivalent to 2 calories. The molecular heat at constant pressure is thus 2 cal. more than that at constant volume.

From the kinetic theory of gases it can be deduced that the molecular heat of a monatomic gas at constant pressure is 5 cal. At constant volume it must be 2 cal. less, or 3 cal. The ratio of these quantities of heat is therefore $5:3=1.66$. When the molecules of the gas consist of more than one atom, more heat is absorbed for the same rise of temperature, because heat is then used not only for the movement of the molecules, but also for that of the atoms in the molecule. The ratio then becomes $5+m:3+m$, if m is the additional heat. The resulting ratio is thus less than 1.66. By determining this ratio (which can be found from the velocity of propagation of sound in the gas by a well-known physical formula) we can ascertain whether the gases are monatomic or poly-atomic. For the gases of this group the ratio was found to be 1.66, proving that their molecules contain only one atom.

Compounds of Nitrogen and Hydrogen.

112. Until recent years only one compound of hydrogen and nitrogen has been known, viz., *ammonia*, NH_3. At present, however, we know five: the others being *hydrazine*, N_2H_4, *hydrazoic acid*, N_3H, and the *compounds of the latter with ammonia and with hydrazine* ($NH_3 \cdot N_3H$ and $N_2H_4 \cdot N_3H$). Of these five compounds, however, ammonia is by far the most important.

AMMONIA.

The material now used for obtaining ammonia is the "ammonia liquor" of the gas-factories. The gases that are given off in the dry distillation of coal are passed through water, which dissolves the ammonia.

In order to obtain a pure ammonia, the ammonia liquor is heated with milk of lime and the expelled ammonia is led into concentrated sulphuric acid. In this way crystallized ammonium sulphate is obtained. It is purified by recrystallization and again distilled with lime to recover the free ammonia.

Ammonia can be prepared synthetically by the following methods, which are as yet, however, without any industrial importance. The direct synthesis from the elements was given above (§ 107). There are also examples of its formation by the direct decomposition of its compounds. Thus we obtain it by heating the ammonia compounds of certain salts, as $x\mathrm{CaCl_2}\cdot y\mathrm{NH_3}$ and $x\mathrm{AgCl}\cdot y\mathrm{NH_3}$. A number of organic compounds yield nitrogen in the form of ammonia on heating. Moreover, ammonia results from the action of hydrogen on certain nitrogen compounds, as, for example, when nitric acid, HNO_3, comes in contact with nascent hydrogen (generated from zinc or iron filings and dilute sulphuric acid), or when a mixture of nitric oxide, NO, with hydrogen is passed over platinum black:

$$2NO+5H_2=2NH_3+2H_2O.$$

The formation of ammonia by the action of free nitrogen on hydrogen compounds has not been brought about, but the gas can be produced by the interaction of a hydrogen compound with a nitrogen compound. An illustration of this is the decomposition of magnesium nitride (§ 107) by water:

$$Mg_3N_2+3H_2O=2NH_3+3MgO.$$

The putrefaction of organic matter (fæces, urine, etc.) evolves ammonia. By the action of electric sparks on moist air ammonium nitrate is produced. These last two methods of formation are responsible for the slight traces of ammonia in the air.

Physical Properties.—Ammonia at ordinary temperatures is a gas with a characteristic odor, that excites one to tears. Its specific gravity is 8.5 (H = 1) or 0.589 (air = 1); 1 l. NH_3 at 0° and 760 mm. pressure weighs 0.76193 g. It can be easily liquefied; it boils at $-33.7°$ and becomes solid at $-75°$; it then forms white translucent crystals. It is extremely soluble in water; at 0° and normal pressure 1 vol. H_2O dissolves 1148 vols., or 0.875 parts by weight, of NH_3. The specific gravity of the solution of ammonia in water grows smaller as the concentration increases. The evaporation of liquid ammonia involves a considerable depression of temperature. This is the principle of most of the ice-machines now in use.

Chemical Properties.—The characteristic property of this compound is that *it combines with acids directly to form salts:*

$$NH_3 + HCl = \underset{\text{Ammonium chloride.}}{NH_4Cl}. \qquad NH_3 + HNO_3 = \underset{\text{Ammonium nitrate.}}{NH_4NO_3}.$$

$$2NH_3 + H_2SO_4 = \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4}.$$

In these salts (which are almost all readily soluble in water) the atomic group NH_4 plays the part of a metal; they correspond in every respect to the compounds KCl, KNO_3, K_2SO_4, etc. The group, or radical, NH_4 has been given a particular name; it is called **ammonium.** More than one attempt has been made to isolate this ammonium, but always in vain. However, when sodium amalgam comes in contact with a concentrated ammonium chloride solution, the mercury swells to a soft spongy mass that rapidly decomposes at ordinary temperatures into ammonia and hydrogen and is in all probability, therefore, ammonium amalgam. If sodium amalgam is allowed to react with ammonium iodide dissolved in liquid ammonia at $-39°$, a hard metallic mass is obtained, which swells with rising temperature because of decomposition into mercury, hydrogen (1 vol.) and ammonia (2 vols.):

$$2NH_4 = 2NH_3 + H_2.$$

The aqueous solution of ammonia reacts strongly basic; so do the moist fumes of ammonia. We must therefore assume that this solution contains a compound NH_4OH, ammonium hydroxide, and hence also the ions NH_4 and OH in analogy with other soluble bases, e.g. potassium hydroxide, KOH. As a matter of fact, however, the solution of ammonia conducts the electric current much more poorly than a solution of sodium hydroxide of equivalent concentration (§ 234). Ammonium hydroxide has not yet been isolated. When the solution of it is evaporated, NH_4OH splits up into NH_3 and H_2O. Concordant herewith is the well-known fact that ammonia can be entirely expelled from its aqueous solution by boiling.

Ammonia does not burn in the air but does in oxygen; in addition to water and nitrogen traces of ammonium nitrite, NH_4NO_2, and nitrogen dioxide, NO_2, are also formed. A mixture of ammonia and oxygen explodes violently when it is ignited. The oxygen conveyed by soil bacteria may also cause the oxidation of ammonia, producing nitric acid. Chlorine takes fire when passed into ammonia, forming nitrogen, N_2, and hydrochloric acid; the latter then unites with the remaining ammonia to form sal ammoniac, NH_4Cl. The hydrogen of ammonia is replaceable by metals. Magnesium, e.g. burns in ammonia, forming magnesium nitride, Mg_3N_2. When ammonia is conducted over hot potassium or sodium, potassium amide, NH_2K, or sodium amide, NH_2Na, is formed. These and analogous metal compounds are decomposed by water, yielding ammonia again and also metal oxide or hydroxide. At high temperatures (produced by induction sparks) ammonia splits up almost completely into its elements, the volume being doubled:

$$\underset{\text{2 vols.}}{2NH_3} = \underset{\text{1 vol.}}{N_2} + \underset{\text{3 vols.}}{3H_2}.$$

On the other hand, nitrogen and hydrogen can unite to form ammonia under the influence of induction sparks (§ 107). Equilibrium is reached when 2% of ammonia is formed. This is the reason why ammonia cannot be split up by electric sparks to more than 98%:

$$\underset{2\%}{2NH_3} \rightleftarrows \underbrace{N_2 + 3H_2}_{98\%}.$$

Nevertheless N_2+3H_2 can be completely converted into $2NH_3$ by induction sparks if the gas mixture is brought in contact with an acid, for by this means ammonia is constantly withdrawn from the gaseous system $N_2+3H_2 \rightleftarrows 2NH_3$; the remaining gas mixture will therefore form new NH_3 in order to restore the equilibrium, and so on, until all the nitrogen and hydrogen have combined.

113. *Composition of Ammonia.*—If an aqueous ammonia solution (to which has been added a little sodium chloride to aid conduction) is subjected to electrolysis, nitrogen and hydrogen are generated in the volume ratio of 1:3; from this it follows that the molecule must contain 3 H-atoms to every 1 N-atom, i.e. the empirical formula is NH_3. Since the specific gravity of ammonia gas is 8.5 ($O=16$), the molecular weight is 17, which corresponds to the above formula.

HYDRAZINE, OR DIAMIDE, N_2H_4.

114. This compound can be obtained by the action of sulphurous acid on potassium nitrite, which yields a compound $K_2SO_3N_2O_2$, nitrosylpotassium sulphite. When the latter is reduced in aqueous solution by sodium amalgam, hydrazine is formed:

$$K_2SO_3N_2O_2 + 3H_2 = N_2H_4 + K_2SO_4 + H_2O.$$

It is far easier to prepare hydrazine from some organic substances, but these methods fall outside of the scope of this book.

By fractional distillation of the aqueous solution the hydrate $N_2H_4 \cdot H_2O$ is obtained, which boils constant at 118.5°; it is a liquid at ordinary temperatures and freezes below −40°.

Lobry de Bruyn showed that the molecule of water can be removed by treatment with barium oxide and that the *free hydrazine* can be obtained in the pure state by distillation under reduced pressure. This substance is liquid at ordinary temperatures, congeals at 1.4° and boils under ordinary pressure at 113.5°. Sp. g. = 1.014 at 15°. It unites with water to form the above hydrate with the evolution of heat. Both the free hydrazine and its aqueous solution have a strong reducing action. The former gradually oxidizes in the air, reacts vigorously with the halogens, etc. The aqueous solution precipitates the metals from solutions of salts of copper, mercury, silver, etc., at ordinary temperatures.

Hydrazine, like ammonia, unites with acids directly to form salts; it can take up either one or two molecules of a monobasic acid, $N_2H_4 \cdot HCl$ and $N_2H_4 \cdot 2HCl$ being both known. The aqueous solution of hydrazine is strongly basic. Its salts are easily soluble in water, excepting the sulphate, $N_2H_4 \cdot H_2SO_4$, which is rather difficultly so.

HYDRAZOIC ACID, N_3H.

115. This interesting compound, like the preceding one, was first discovered by Curtius as a product of organic compounds. It can be prepared by a purely inorganic method, viz. by passing nitrous oxide over sodium amide, $NaNH_2$, at a high temperature (§ 111),

$$2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3,$$

or by treating hydrazine sulphate (§ 114) with nitrous acid:

$$3N_2H_4 \cdot H_2SO_4 + 6KNO_2 + 3H_2SO_4 = \\ 2N_3H + 8H_2O + 6KHSO_4 + 2O + 2N + 2N_2O.$$

An aqueous solution of the free acid is best obtained by distilling lead hydrazoate, $Pb(N_3)_2$, with dilute sulphuric acid. By fractional distillation of this solution the pure acid can be obtained.

Pure hydrazoic acid is a liquid with a penetrating, unbearable odor; it boils at 37° and is extremely explosive, even in aqueous solution.

It is a strange fact that hydrazoic acid displays more or less analogy with the hydrogen acids of the halogens; it forms, like them, difficultly soluble salts of silver, mercury (ous) and lead. These are, however, soluble in strong mineral acids. They are also very explosive, hence extremely dangerous, the sodium salt being the least so. An aqueous 1% solution of the acid is only 0.008 ionized; it is thus a rather weak acid; it gives off hydrogen in contact with many metals, e.g. Zn, Fe, Cd, and Mg. It is characteristic of the metal hydrazoates (or "azides") that they crystallize anhydrous and yield the pure metal when heated.

Compounds of Nitrogen with the Halogens.

116. When chlorine gas is allowed to act on a concentrated solution of ammonium chloride, most conveniently by inverting a flask full of chlorine over the warm (30°–40°) solution, oily drops are formed, which are best collected in a leaden saucer placed under the mouth of the flask. These drops contain some hydrogen as well as nitrogen and chlorine. By treating with chlorine once more pure **nitrogen trichloride,** NCl_3, is obtained as a yellowish oil with a disagreeable pungent odor and a specific gravity of 1.65. This is one of the most dangerous of substances, because it explodes in a most violent manner, not only on contact with certain organic substances (e.g. turpentine), but very often spontaneously. It dissolves in carbon disulphide, benzene and other solvents, forming yellow solutions. These solutions are relatively harmless; they decompose in the sunlight.

Concentrated hydrochloric acid decomposes nitrogen trichloride according to the equation:

$$NCl_3 + 4HCl = NH_4Cl + 3Cl_2;$$

aqueous ammonia also breaks it up in a similar way:

$$NCl_3 + 4NH_3 = 3NH_4Cl + N_2.$$

Nitrogen trichloride is strongly endothermic:

$$N + 3Cl - NCl_3 = -41.9 \text{ Cal.}$$

117. Nitrogen Iodide.—If a solution of iodine in potassium iodide is mixed with ammonia solution, a precipitate is usually obtained of the composition NI_2H; if the conditions are slightly altered another compound, $N_2I_3H_3$ (i.e. NH_3+NI_3), is deposited which breaks up on continued treatment with water into ammonia and nitrogen tri-iodide. These compounds are likewise very explosive.

Another method is to digest pulverized iodine with ammonia water. The product so obtained is still more explosive, often exploding even when damp or when it is being washed with water or by the action of hydrochloric acid. In the presence of ammonia solution it is stable.

Nitrogen iodide is decomposed by dilute hydrochloric acid, forming ammonia and chlorine iodide:

$$NH_2I+HCl=NH_3+ICl.$$

Nitrogen iodide is also decidedly endothermic.

Hydroxylamine, NH_2OH.

118. Hydroxylamine is a reduction product of many oxygen compounds of nitrogen intermediate to the formation of ammonia; e.g. it is formed when tin acts on dilute nitric acid. Here the nascent hydrogen effects the reduction:

$$HNO_3+3H_2=NH_3O+2H_2O.$$

It is manufactured by the electrolytic reduction of nitric acid dissolved in sulphuric acid.

LOBRY DE BRUYN succeeded in preparing hydroxylamine in the pure anhydrous condition. He added sodium methylate to a solution of the hydrochloride in absolute (i.e. anhydrous) methyl alcohol, by which a solution of free hydroxylamine in the latter is obtained. This solution is freed from the precipitated sodium chloride by filtration and then the alcohol is removed by distillation, at first under ordinary pressure; the free base, NH_2OH, is then obtained pure by fractionating under diminished pressure. It is a crystalline solid, melting at 30° and boiling at 70° under 60 mm. pressure. When heated in the air, it explodes with a yellow flame.

Hydroxylamine is easily soluble in water; its solution reacts strongly alkaline. It forms salts in the same way as ammonia, i.e. by direct addition of the acid: $NH_2OH \cdot HCl$, $NH_2OH \cdot HNO_3$, etc. These salts are rather stable; the hydrochloride, however, must be preserved over lime, else it slowly decomposes, for the following reason. The salt is split up to a very small degree into hydrochloric acid and hydroxylamine. Now free hydrochloric acid accelerates catalytically the decomposition of the salt. When, however, the hydrochloric acid is absorbed by the lime, the decomposition becomes so slow that it is imperceptible. The free hydroxylamine and its aqueous solution are somewhat unstable, especially in the presence of alkalies; it decomposes easily into ammonia, water and nitrogen.

A further characteristic of hydroxylamine is its great reducing power; it precipitates reddish-yellow cuprous oxide from an alkaline copper solution at ordinary temperatures, even when strongly diluted; mercuric chloride, $HgCl_2$, is reduced to calomel, Hg_2Cl_2; silver nitrate to silver, etc.

The following reaction is also peculiar: A solution of ferrous sulphate is precipitated with an excess of sodium hydroxide and warmed; if hydroxylamine (or one of its salts) is now added to the green ferrous hydroxide, red ferric hydroxide is formed very quickly, the hydroxylamine being reduced in this alkaline solution to ammonia. On acidifying, an acid solution of a ferric salt is obtained; if this is treated with a hydroxylamine salt, it is suddenly decolorized because of reduction to ferrous salt, the hydroxylamine being now in the oxidized condition in the acid solution.

Compounds of Nitrogen with Oxygen.

Those included under this title are: *nitrous oxide*, N_2O; *nitric oxide*, NO; *nitrogen trioxide*, or nitrous anhydride, N_2O_3; *nitrogen dioxide*, NO_2, or *tetroxide*, N_2O_4, and *nitrogen pentoxide*, or nitric anhydride, N_2O_5.

NITROUS OXIDE, N_2O.

119. This compound cannot be obtained directly from its elements; the ordinary method of preparation consists in heating ammonium nitrate to about 250°:

$$NH_4NO_3 = N_2O + 2H_2O.$$

This method is analogous to that of preparing nitrogen from ammonium nitrite (§ 105). If the nitrate is heated above 250°, the gaseous product partially decomposes.

Physical Properties.—Nitrous oxide is a colorless and odorless gas, which when liquefied boils at $-87°$ and solidifies at $-102°$. The evaporation of the liquid produces a great depression in the temperature, which may even reach $-140°$ under reduced pressure. Its specific gravity is 1.52 (based on air), or 21.89 for $H=1$. 1 l. N_2O at 0° and 760 mm. pressure weighs 1.9657 g. It is rather soluble in water (1 vol. H_2O dissolves 1.305 vol. N_2O at 0°); hence it must be collected over hot water. In alcohol it is still more soluble.

Chemical Properties. — Nitrous oxide supports combustion. Phosphorus, carbon and a glowing splinter burn in it as in oxygen. A mixture of nitrous oxide and hydrogen explodes like detonating-gas when it is ignited, only not quite so loud. These properties might lead one to confuse it with oxygen on a superficial examination. However, it is very easily distinguished from the latter by the fact that it gives no red fumes when mixed with nitric oxide (§ 120) and always leaves residual gas (nitrogen) after a combustion. A faintly burning piece of sulphur is moreover extinguished by nitrous oxide.

Nitrous oxide is endothermic: $2N+O-N_2O=-17.7$ Cal.

Berthelot has made the general observation that endothermic substances can suffer an explosive decomposition; in this case this may be brought about by touching off the gas with fulminating mercury. It is easy to explain Berthelot's observation. When an endothermic substance decomposes, heat is evolved. Now, we saw in §§ 12 and 104 that chemical reactions are accelerated in a very high degree by rise of temperature. Suppose that a sudden decomposition is caused at a certain point in a mass of an endothermic compound. The heat given off raises the temperature of the surrounding molecules and they too split up suddenly, evolving still more heat, and so on. The whole mass will thus reach a condition of sudden decomposition, that is, it will explode. To bring this about it is only necessary that the first impulse be vigorous enough for the sudden decomposition of so many molecules that the heat evolved is sufficient to raise the surrounding ones to the temperature of decomposition.

Composition.—Under the protracted action of induction sparks the gas splits up into a mixture of nitrogen and oxygen, the volume of which is half again as great as that of the nitrous oxide. When potassium and sodium are burned in the gas, potassium and sodium oxides respectively are formed, together with nitrogen; the gas volume after cooling is unchanged. Both of these observations point to the same formula, N_2O, and this is confirmed by the fact that the relative density of the gas, which should theoretically be

$$\frac{2\times 14+16}{2}=22(H=1),$$

was found to be 21.89.

NITRIC OXIDE, NO.

120. This gas is only obtained by the reduction of nitric or nitrous acid. The ordinary method of preparation is by allowing copper to act on nitric acid or else by covering copper (in the form of thin sheets) with a saturated solution of saltpetre and adding concentrated sulphuric acid drop by drop (§ 127):

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO.$$

In this reaction the hydrogen, which would be expected to be given off, reduces another portion of the acid.

In order to prepare nitric oxide by the reduction of nitric acid or a nitrate a boiling-hot solution of ferrous chloride, $FeCl_2$, in hydrochloric acid is found very satisfactory; the ferrous chloride is converted into the ferric chloride, $FeCl_3$, by the reaction:

$$HNO_3+3FeCl_2+3HCl=3FeCl_3+2H_2O+NO.$$

Perfectly pure nitric oxide is obtained by treating a mixture of yellow prussiate of potash and potassium nitrite with acetic acid:

$$\underset{\text{Yellow prussiate.}}{2K_4Fe(CN)_6}+\underset{\text{Pot. nitrite}}{2KNO_2}+\underset{\text{Acet. acid.}}{4C_2H_4O_2}=\underset{\text{Red prussiate.}}{K_6Fe_2(CN)_{12}}+\underset{\text{Pot. acetate}}{4KC_2H_3O_2}+2H_2O+2NO.$$

Physical Properties.—Nitric oxide is a colorless gas, whose specific gravity has been found to be 1.039 (air = 1). It can be condensed to a blue liquid, which boils under ordinary pressure at

$-153.6°$. The critical temperature is $-93.5°$, the critical pressure 71.2 atm. It is not very soluble in water, but dissolves easily in a solution of ferrous sulphate, $FeSO_4$; strange to say, this solution is quite dark brown in color, although the ferrous salt solution is pale green and nitric oxide colorless. It is probable that this brown color is due to the formation of a complex ion of Fe and NO.

Chemical Properties.—It is characteristic of this gas, above all other properties, that it combines with oxygen immediately, forming nitrogen dioxide, a reddish-brown gas. On heating it with hydrogen no explosion occurs; the mixture burns with a white flame, forming water and nitrogen. If burning phosphorus is introduced into the gas, it continues to burn; a lighted candle is, however, extinguished; sulphur and charcoal do not burn in it either. A mixture of nitric oxide and carbon disulphide burns with an intensely luminous blue flame, that is very rich in chemically effective rays.

Nitric oxide is a strongly endothermic compound; it can be made to explode by fulminating mercury (§ 119). According to § 103 NO must be formed at a high temperature. NERNST proved that the reaction $N_2+O_2 \rightleftarrows 2NO$ accords strictly with the law of mass-action (§ 49); from whichever side one starts, the results are in agreement with those calculated, assuming both reactions to be bimolecular. The formation of NO is perceptible as low as 1500°; at 2200° about one volume per cent is formed.

The formation and the decomposition of NO are much slower than in the case of ozone. Accordingly a short heating of air, followed by a rapid cooling, produces ozone, while a slower heating and cooling yield NO, ozone being broken up during the extended period of cooling. The following experiment illustrates this: When moist air is directed with a velocity of less than 7 m. per sec. against an incandescent NERNST filament (§ 291) NO is formed; a more rapid current gives ozone.

Composition.—When sodium is heated in contact with a measured amount of nitric oxide, sodium oxide and nitrogen are formed; the latter takes up exactly half the volume of the original gas. The specific gravity of nitric oxide is 15 ($H=1$), hence its molecular weight is 30. According to the above decomposition the gas contains one atom of nitrogen (14 parts by weight). There remain for the oxygen, therefore, 16 parts by weight, i.e. just one atom. Hence the formula is NO.

Since nitrogen is trivalent or quinquivalent (the latter in ammonium salts, e.g. NH_4Cl) and oxygen is bivalent, it must be assumed that there is a free valence bond in NO, i.e. -N=O. The same applies to NO_2. Free bonds like these are very rare.

Nitrous Anhydride, N_2O_3.

121. This compound is only known at low temperatures. It is obtained as a blue liquid when nitric oxide is led into the liquid tetroxide, N_2O_4, at −21°. In the solid state it is pale blue and melts at −111° to a dark-blue liquid. In the gaseous state the compound dissociates almost completely, even at a low temperature, into NO_2 and NO. By the action of arsenious anhydride, As_2O_3, on nitric acid (sp. g. 1.3) a gas mixture is formed which has almost exactly the composition N_2O_3, i.e. $NO_2 + NO$.

NITROGEN DIOXIDE AND TETROXIDE, NO_2 AND N_2O_4.

122. Nitrogen dioxide is formed from nitric oxide plus oxygen, or more conveniently by heating well-dried lead nitrate:

$$Pb(NO_3)_2 = PbO + O + 2NO_2.$$

When so prepared it is a very deep-brown gas. On leading it into a strongly cooled vessel it condenses to a bright-yellow liquid, which solidifies at −20° to colorless crystals, that melt at −12°. The color becomes darker on warming and at +26° the liquid begins to boil, changing back again into the brown gas. The vapor density of this gas at 26° is found to be 38.0, while that calculated for N_2O_4 is 45.9 and that for NO_2 22.9 $(H=1)$. Since the value found is between the two, it may be assumed that at this temperature the vapor consists partly of N_2O_4 molecules and partly of NO_2 molecules. A simple calculation indicates the percentage of the former to be 34.4%. As the temperature rises, the vapor density steadily decreases till about 150° is reached, when it becomes constant at 22.9. There is evidently complete dissociation of N_2O_4 molecules in this case,

$$\underset{1\text{ vol.}}{N_2O_4} \rightleftarrows \underset{2\text{ vols.}}{2NO_2},$$

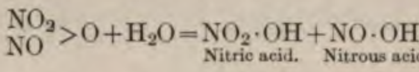
and, inasmuch as the color of the gas grows darker, we must suppose that NO_2 is dark brown, while N_2O_4 is colorless, which is true of the latter in the solid state. This supposition is supported by the fact that not only can the degree of dissociation be estimated from the intensity of the color, but that it can even be measured quantitatively in this way.

According to § 51 the equilibrium between the two gases is expressed by the equation

$$P-x=kx^2,$$

where P is the total pressure of the gas mixture and x that of the dioxide, k being a constant. From this equation it follows that the dissociation (at a constant temperature) depends on the pressure (§ 51), which has been shown to be the case. This also follows from the theorem of Le Chatelier (§ 102).

On bringing nitrogen tetroxide in contact with water or, better, with alkalies, nitrous and nitric acids are formed; we may therefore consider it as a mixed anhydride of these two acids:



$$\begin{matrix}NO_2\\NO\end{matrix}\!>O+H_2O=\underset{\text{Nitric acid.}}{NO_2\cdot OH}+\underset{\text{Nitrous acid.}}{NO\cdot OH}.$$

Both NO_2 and N_2O_4 possess strong oxidizing power; many substances burn in their vapor; they precipitate iodine from soluble iodides.

The *composition of nitrogen dioxide* follows from its synthesis-equation, $2NO+O_2$, and from the vapor density.

Nitrogen Pentoxide, N_2O_5.

123. This compound can be obtained by the action of chlorine on silver nitrate or by distilling fuming nitric acid with phosphorus pentoxide. It is a colorless crystalline solid. It melts at 30°, and at 45–50° breaks up, giving off brown fumes. If the heating takes place rather rapidly the decomposition is explosive in nature; sometimes a spontaneous explosion takes place, hence it can not be kept long.

As nitrogen pentoxide is strongly endothermic, its spontaneous explosion must be explained in the same way as is indicated in § 119. Only we must conclude in this case that the decomposition at ordinary temperatures is vigorous enough to sufficiently heat the neighboring molecules.

It unites with water, forming nitric acid with the evolution of much heat. As might be expected, it has strongly oxidizing properties. Phosphorus and potassium, for instance, burn with great brilliance in the slightly warmed anhydride.

The composition of nitrogen pentoxide is ascertained by heating with powdered copper; the amount of nitrogen evolved corresponds to the formula N_2O_5.

Oxygen Acids of Nitrogen.

124. Four acids of nitrogen are known: *hyponitrous acid,* $H_2N_2O_2$; *nitrohydroxylaminic acid,* $H_2N_2O_3$; *nitrous acid,* HNO_2; *nitric acid,* HNO_3. The nitrous acid is known only in dilute aqueous solution; nitrohydroxylaminic acid is known only in its salts; but the others are known in the pure state.

Only certain ones of the above nitrogen oxides can be regarded as acid anhydrides. The pentoxide is undoubtedly one and the tetroxide may be considered as a mixed anhydride of nitric and nitrous acids (§ 122). Nitrogen trioxide gives a solution of nitrous acid when mixed with water at a low temperature; however, this solution undergoes a decomposition slowly at ordinary, more rapidly at higher, temperatures, nitric acid and nitric oxide being formed:

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The acid corresponding to nitric oxide, NO, is nitrohydroxylaminic acid. However no one has yet been able to obtain this acid from nitric oxide and water. The same is true for nitrous oxide, to which hyponitrous acid corresponds.

Hyponitrous Acid, $H_2N_2O_2$.

125. This acid is formed when nitrogen trioxide is introduced into a methyl-alcoholic solution of hydroxylamine. After neutralization the difficultly soluble yellow silver hyponitrite, $Ag_2N_2O_2$, can be precipitated from the solution by silver nitrate. From this salt the free acid is obtained by treating it with ether saturated with hydrochloric acid gas and evaporating the ether, whereupon it is left in the form of white flaky crystals. These are very explosive and dissolve very easily in water. The freezing-point depression of the aqueous solution shows that the molecular formula is $H_2N_2O_2$. On warming the aqueous solution the acid breaks up almost wholly into nitrous oxide and water. When the acid is set free (by the addition of an excess of silver hyponitrite to cold dilute hydrochloric acid) it does not liberate iodine from potassium iodide at once; the reaction is delayed for a time, probably on account of a decomposition, by which nitrous acid is formed.

Hyponitrous acid belongs to the class of weak acids; its aqueous solution is a poor conductor. Both neutral and acid salts of this acid are known.

Nitrohydroxylaminic Acid, $H_2N_2O_3$.

This acid does not exist in the free state, being known only in salts. Its sodium salt is obtained by mixing an alcoholic solution containing sodium alcoholate and hydroxylamine with ethyl nitrate:

$$\underset{\text{Ethyl Nitrate}}{C_2H_5ONO_2} + NH_2OH = C_2H_5OH + H_2N_2O_3.$$

The alcoholate is added in order to convert the free acid directly into its sodium salt. If the attempt is made to liberate it by adding a stronger acid, it is immediately decomposed according to the equation:

$$Na_2N_2O_3 + 2HCl = 2NaCl + 2NO + H_2O.$$

The sodium salt, heated in aqueous solution, gives sodium nitrate and nitrous oxide. When the sodium salt is heated dry until it begins to melt, it is decomposed into nitrite and hyponitrite:

$$2Na_2N_2O_3 = 2NaNO_2 + Na_2N_2O_2.$$

NITROUS ACID, HNO_2.

126. It was remarked above that this acid is only known in dilute solution at ordinary or low temperatures; its salts are, however, stable. In order to prepare them we usually employ potassium or sodium nitrate, which gives off oxygen when heated and is converted into nitrite. This decomposition takes place more readily if lead is added during the heating as a reducing agent:

$$2KNO_3 = 2KNO_2 + O_2.$$

Its salts are all easily soluble in water, with the exception of silver nitrite, $AgNO_2$, which is rather difficultly soluble at ordinary temperatures; it is obtained as a yellow crystalline precipitate, when not too dilute solutions of silver nitrate are mixed with a nitrite.

The addition of strong sulphuric acid to a nitrite at once produces red fumes; in this way a nitrite can be distinguished from a nitrate, for the latter does not produce them. It may be assumed that in this reaction free nitrous acid is primarily formed; this is, however, broken up directly into water and nitrogen trioxide, the latter of which at once splits up again into NO_2+NO; thereupon the nitric oxide unites immediately with the surrounding oxygen to form dioxide. The red fumes thus consist solely of nitrogen dioxide, NO_2.

On treating a very dilute nitrite solution with the equivalent amount of sulphuric acid a dilute solution of free nitrous acid is obtained. This solution can act either oxidizing or reducing. As examples of the former action we have the liberation of iodine from a solution of potassium iodide, the oxidation of sulphurous acid in dilute solution to sulphuric acid, the oxidation of ferrous sulphate, $FeSO_4$, to ferric sulphate, $Fe_2(SO_4)_3$, and the conversion of the yellow to the red prussiate of potash. In all of these cases lower oxides of nitrogen, chiefly nitric oxide, are formed. An example of its reducing action (in which nitrous acid is oxidized to nitric acid) is the bleaching of potassium permanganate, $KMnO_4$, in sulphuric acid solution:

$$2KMnO_4+5HNO_2+3H_2SO_4=K_2SO_4+2MnSO_4+5HNO_3+3H_2O.$$

This last reaction offers a means of determining quantitatively (volumetrically, see § 93) the strength of a dilute solution of nitrous acid.

NITRIC ACID, HNO_3.

127. This is the best known acid of nitrogen. It is manufactured on a large scale, since its uses are many and varied; in the organic dyestuff industry, for example, large quantities are employed. The commercial process of manufacture depends on the decomposition of Chili saltpetre, $NaNO_3$, by strong sulphuric acid:

$$NaNO_3+H_2SO_4=NaHSO_4+HNO_3$$

One of the simplest methods of carrying it out is as follows:

In the cast-iron retort (*C*, Fig. 38), saltpetre and sulphuric acid (chamber-acid) are mixed in proportions corresponding to the above equation, a slight excess of sulphuric acid, however, being added, because this makes the residue easier to remove from the retort. The retort is connected with a row of earthenware bottles (*EE′*) containing a little water. These receive the distilled acid. The last bottle connects with a coke tower through which water is trickling down to dissolve the uncondensed acid vapor. By this process a liquid of a specific gravity of 1.35 and containing 60% acid is obtained. If the saltpetre is previously dried and concentrated sulphuric acid is used, a nitric acid of sp. g. 1.52 and almost 100% pure can be obtained.

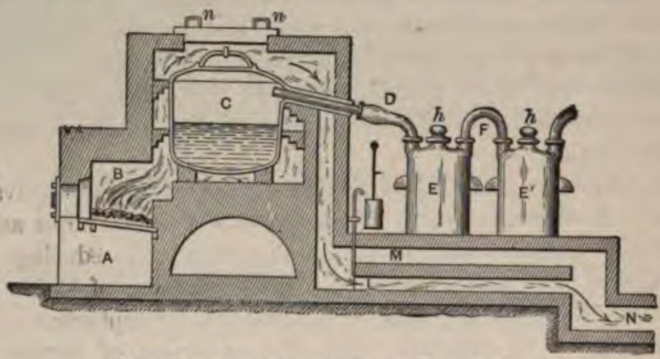


FIG. 38.—MANUFACTURE OF NITRIC ACID.

In some cases two molecules of saltpetre are used to one of sulphuric acid. If heat is moderately applied, the reaction proceeds according to the above equation, but on heating to a higher temperature the acid sodium sulphate that is formed acts on the second molecule of nitrate, also forming nitric acid:

$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3.$$

A large part of the nitric acid, however, dissociates at the same time as follows:

$$2HNO_3 = 2NO_2 + H_2O + O.$$

The NO_2-fumes dissolve in the distillate. The liquid thus obtained is red and its specific gravity is 1.52–1.54; it fumes strongly in the air and is known as "*red fuming nitric acid.*"

For some years the distillation of saltpetre with sulphuric acid has been carried on in a vacuum. The yield of acid in such a case approaches closely to the theoretical and the product obtained is entirely free from nitrous fumes.

An entirely distinct method for the industrial preparation of nitric acid was invented a few years ago by Birkeland and Eyde. They make use of the nitrogen and oxygen of the atmosphere. The problem of making nitric acid from this rather inexhaustible source has been studied for many years, but these men are the first to handle it with success on a commercial scale. The solution of the problem became a really pressing matter, because the principal material for the preparation of nitrogen compounds, Chili saltpetre, bids fair to be exhausted in thirty-five years, and saltpetre has not only a large significance in the industrial world but a still larger one in agriculture as a nitrogenous fertilizer.

The method of Birkeland and Eyde is based on the long established fact that oxides of nitrogen are formed in an electric arc burning in the air. The reason why previous investigations did not succeed lies in the fact that an ordinary electric arc has too small a volume, and therefore, cannot let a sufficient quantity of air pass. This difficulty is now obviated by mounting the arc between the poles *PP* of a very powerful electric magnet *EE* (Fig. 39). The arc is produced between two hollow bars of copper, which are kept cool by circulating water in them. When an alternate current is used for producing the arc, the latter spreads out in the shape of a flat disc that reaches a diameter of 2 m. in the industrial form of the apparatus; the tension employed is 5000 volts. This flame disc is inclosed in a box through

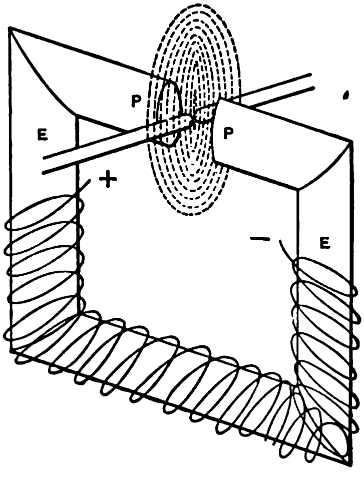


Fig. 39.—Diagram of Birkeland and Eyde Nitric Acid Apparatus.

which a rapid current of air is forced, and the contact with the flame is sufficient to form as high as 2% of NO. This nitric oxide combines with more oxygen to form NO_2, which is absorbed in towers resembling the Gay-Lussac tower of a sulphuric acid plant. With water it then forms nitric acid and nitrous acid:

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

The latter yields NO_2 and NO, however, when the liquid becomes more concentrated:

$$2HNO_2 = H_2O + NO_2 + NO.$$

NO is once more converted into NO_2 and the NO_2 again gives nitric acid; eventually all is converted into that acid. Instead of marketing sodium nitrate, to duplicate the Chili saltpetre, calcium nitrate is produced by saturating the nitric acid with lime and the resulting calcium nitrate is used for fertilizing and other purposes.

Nitrites are also manufactured directly by leading N_2O_4 into caustic:

$$N_2O_4 + 2KOH = KNO_3 + KNO_2 + H_2O.$$

The nitrate and nitrite are separable by fractional crystallization.

Physical Properties.—Absolute nitric acid, i.e. the compound HNO_3 in the pure state, is prepared by distilling the nearly pure acid of commerce (sp. g. 1.5) with concentrated sulphuric acid *in vacuo.* The liquid distillate has a specific gravity of 1.559 at 0° and becomes solid at −40°; it boils under ordinary pressure at 86°, but with partial decomposition.

Chemical Properties.—Nitric acid, especially when pure, is a rather unstable compound; at ordinary temperatures it is decomposed by sunlight to a slight extent, turning yellow on account of the small amount of nitrogen dioxide formed. At an elevated temperature the acid also breaks up, decomposition into nitrogen dioxide, water, and oxygen being complete at 260°.

When strong nitric acid is subjected to repeated distillation under atmospheric pressure, its boiling-point gradually rises, while the acid becomes proportionately weaker, until finally a 68% acid is obtained, which boils constant at 120.5°. The same mixture is obtained when one starts with dilute acid and distils it. In both cases the boiling-point of the original liquid is lower than that of the product; it rises during the boiling to a maximum at 120.5°. We have here, therefore the case of a liquid mixture with a maximum boiling-point, which is discussed in ORG. CHEM., § 22. The mixture of hydrogen chloride and water also has a maximum boiling-point (110°).

Nitric acid is very extensively ionized in aqueous solution; it is one of the strongest acids known.

When it comes in contact with metals, the salts of nitric acid (nitrates) are formed, but without any evolution of hydrogen, since part of the acid present is reduced by the nascent hydrogen. The nitrates are all easily soluble in water. The action of nitric acid on the metals is not the same in all cases. It does not attack gold or platinum. Silver, mercury, and copper are only imperceptibly dissolved at ordinary temperatures, but on warming they dissolve with the evolution of nitric oxide. This and the other NO-compounds are powerful catalyzers in the dissolving of the above-named metals, for nitric acid which is perfecty free from them does not dissolve these metals, while the reaction immediately begins as soon as a little of these substances is added. It may be supposed that on warming nitric acid traces of NO-compounds are formed, which together with the elevation of the temperature accelerate the reaction. Iron, zinc, and magnesium reduce nitric acid to nitrous oxide and even to ammonia. Under the action of iron filings and dilute sulphuric acid the reduction of nitric acid to ammonia in dilute solution is quantitative. There are also various denitrifying bacteria known, *Bac. pyocyaneus* being the best studied of them.

Nitric acid frequently acts as a powerful oxidizing agent, especially at an elevated temperature If sulphur is boiled with it, the sulphur is converted to sulphuric acid, similarly phosphorus to phosphoric acid. A glowing piece of charcoal dropped upon the concentrated acid continues to burn with a bright glow. In all these cases the highest oxidation stages are formed. Nitric acid is used particularly in the organic branches of chemical industry.

The *composition* of nitric acid can be deduced from that of its anhydride. A weighed amount of the latter is introduced into water; nitric acid is formed, which is neutralized with baryta water. By evaporation it is possible to determine how many parts by weight of barium oxide, BaO, combine with the anhydride. It is found that 153.2 parts (=1BaO) combine with 108.08 parts (=$1N_2O_5$) of the anhydride; the formula of barium nitrate thus becomes $Ba(NO_3)_2$, hence that of nitric acid itself must be HNO_3.

Derivatives of the Nitrogen Acids.

128. In discussing the manufacture of sulphuric acid (§ 86) we already referred to the **chamber crystals,** HSO_5N. They are formed in the lead chambers in case not enough steam is supplied. The following equation expresses the action that takes place:

$$2SO_2+N_2O_4+O+H_2O=2SO_5NH.$$

The ordinary method of preparing this substance is by conducting carefully dried sulphurous oxide into cooled fuming nitric acid:

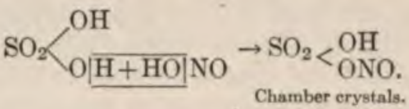
$$SO_2+HNO_3=SO_5NH.$$

The crystalline mass obtained is spread out on porous earthenware to allow the adhering liquid to be absorbed.

The chamber crystals have the appearance of a coarse crystalline, colorless mass; they melt at 73°. They are at once decomposed by water into sulphuric and nitrous acids:

$$SO_5NH+H_2O=H_2SO_4+HNO_2.$$

For this reason the compound is considered as the *mixed anhydride of sulphuric and nitrous acids.* According to § 90 the structure $SO_2{<}\begin{matrix}OH\\OH\end{matrix}$ can be ascribed to sulphuric acid; to nitrous acid the structure HO-NO, since a hydroxyl group is assumed (§ 129) to exist in it. For the chamber crystals we therefore have

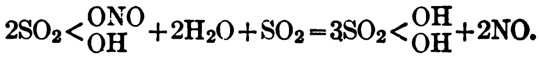


$$SO_2{<}\begin{matrix}OH\\O\boxed{H+HO}NO\end{matrix} \rightarrow SO_2{<}\begin{matrix}OH\\ONO.\end{matrix}$$

Chamber crystals.

Since the atomic group NO is known as *nitrosyl,* the rational name for the compound is *nitrosyl sulphuric acid.*

Concentrated sulphuric acid dissolves nitrosyl sulphuric acid without change. This solution is very stable; it can be distilled without decomposition. It is formed in the Gay-Lussac tower of the sulphuric acid factory and is called "nitrated acid" or "nitrous vitriol." On dilution with water this solution is not altered until its specific gravity reaches 1.55–1.50 (51°–48° B.); then the nitric oxides begin to escape, especially when warmed. Water and sulphurous oxide act on the nitrated acid, producing the following reaction:

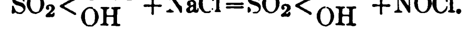


$$2SO_2<\genfrac{}{}{0pt}{}{ONO}{OH}+2H_2O+SO_2=3SO_2<\genfrac{}{}{0pt}{}{OH}{OH}+2NO.$$

This action takes place in the Glover tower.

It is of great importance industrially to be able to determine the amount of nitrogen that the nitrated acid contains. This can be done as follows: The acid is agitated with mercury, whereupon all nitrogen compounds in solution are given off in the form of nitric oxide, and the gas evolved is measured. Another method consists in decomposing the nitrated acid with a large excess of water and titrating the resulting nitrous acid with permanganate (§ 126).

129. Nitrosyl chloride, NOCl, is a reddish-yellow gas at ordinary temperatures; by cooling it can be condensed to a red liquid, that boils at −5.6°. The melting-point lies at −61°. This compound is formed by the direct combination of nitric oxide and chlorine. Bone-black is a good catalyzer of this reaction, making this method of preparation a very satisfactory one. Another method is that of carefully warming chamber crystals with thoroughly dried sodium chloride:



$$SO_2<\genfrac{}{}{0pt}{}{ONO}{OH}+NaCl=SO_2<\genfrac{}{}{0pt}{}{ONa}{OH}+NOCl.$$

Nitrosyl chloride is broken up by water into nitrous and hydrochloric acids:

$$NOCl+H_2O=NO\cdot OH+HCl;$$

hence it may be regarded as the chloride of nitrous acid (§ 130).

On mixing hydrochloric acid with nitric acid a liquid is produced which, in addition to these two acids, contains chlorine and nitrosyl chloride:

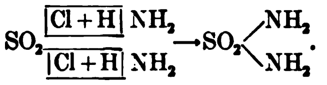
$$HNO_3+3HCl=2H_2O+NOCl+Cl_2.$$

This liquid (in virtue of the free chlorine it contains) dissolves the precious metals, including gold, the "king" of the metals, and therefore bears the name *aqua regia*. It was known even to the alchemists, particularly GEBER, who prepared it by dissolving sal ammoniac, NH_4Cl, in nitric acid.

OTHER NITROGEN COMPOUNDS.

130. In organic chemistry acid derivatives are known which are formed through the substitution of the hydroxyl group by a halogen atom or the amido group, NH_2. The former class are called acid chlorides, the latter amides. Of the inorganic acid chlorides we have already become acquainted with those of sulphuric acid (§ 90). Nitrosyl chloride is also an acid chloride. A few inorganic acid amides will now be discussed briefly.

By the action of ammonia gas on a solution of sulphuryl chloride in chloroform there is formed among other things **sulphamide**, $SO_2(NH_2)_2$.



$$SO_2\begin{array}{l}\boxed{Cl+H}\,NH_2\\ \boxed{Cl+H}\,NH_2\end{array}\rightarrow SO_2\begin{array}{l}\diagup NH_2\\ \diagdown NH_2\end{array}.$$

This compound forms large colorless crystals that are very soluble in water and melt at 81°. It is transformed by alkalies into an **amido-sulphonate**, $SO_2<\substack{OH\\NH_2}$. This acid is very stable, is slightly soluble in water, and crystallizes in colorless rhombic prisms.

Potassium sulphite and potassium nitrite interact to form a crystalline precipitate; this compound, to which is given the formula $N(SO_3K)_3+2H_2O$, is regarded as ammonia in which three hydrogen atoms are replaced by sulpho groups (SO_3K):

$$KNO_2+3K_2SO_3+2H_2O=N(SO_2K)_3+4KOH.$$

It is known as **potassium nitrilosulphonate.** On boiling it for a short time with water, or better, by letting it stand for a day moistened with dilute sulphuric acid, it forms **potassium imidosulphonate:**

$$N(SO_3K)_3+H_2O=NH(SO_3K)_2+KHSO_4.$$

If the boiling is continued for a long period, **amidosulphonic acid** is produced:

$$N(SO_3K)_3 + 2H_2O = NH_2SO_3H + K_2SO_4 + KHSO_4.$$

Similar derivatives of hydroxylamine are also known. The potassium salt of hydroxylamine-disulphonic acid, $HO \cdot N(SO_3K)_2 + 2H_2O$, is formed when solutions of acid potassium sulphite and potassium nitrite are mixed:

$$KNO_2 + 2KHSO_3 = HON(SO_3K)_2 + KOH.$$

By boiling this compound with water hydroxylamine is set free:

$$HON(SO_3K)_2 + 2H_2O = HONH_2 + 2SO_4KH.$$

The amide of nitric acid, **nitramide**, NH_2-NO_2, has so far been obtained only from an organic compound, nitrourethane, $NO_2NH \cdot CO_2C_2H_5$. This amide appears in colorless crystals that melt at 72° with decomposition. The aqueous solution reacts strongly acid. It is a very unstable substance, decomposing on being mixed with copper oxide, powdered glass or the like. It is immediately broken up by alkalies and even by sodium acetate at ordinary temperatures, nitrous oxide and water being formed in the latter case.

PHOSPHORUS.

131. Phosphorus does not occur free in nature, inasmuch as it combines very easily with oxygen. Nevertheless salts of phosphoric acid are widely distributed and occur in large quantities. Tricalcium phosphate, $Ca_3(PO_4)_2$, *phosphorite*, is found in large deposits; other phosphates which are frequently met with are: *apatite*, $3Ca_3(PO_4)_2 + CaCl_2$ (or CaF_2); *wavellite*, $4AlPO_4 + 2Al(OH)_3 + 9H_2O$; and *vivianite*, $Fe_3(PO_4)_2 + 8H_2O$. Phosphates are also found to a small extent in granite and volcanic rocks; when these weather the phosphates enter the soil. About 0.1% of phosphates (calculated as P_2O_5) is present in soil of average fertility. Bones contain a considerable proportion of tricalcium phosphate.

Phosphorus has been known for a long time. In 1674 the alchemist BRAND discovered it at Hamburg by evaporating urine and heating the residue with sand in an earthen retort. SCHEELE first prepared phosphorus from bones by a process which in the main is still employed.

For the *manufacture of phosphorus* bones or phosphorite are used. By treatment with sulphuric acid gypsum and monocalcium phosphate are formed. As the latter remains soluble while the former is precipitated, the phosphate solution is readily poured off.

$$Ca_3(PO_4)_2+2H_2SO_4=\underset{\text{Gypsum.}}{2CaSO_4}+CaH_4(PO_4)_2.$$

On being heated this phosphate loses water and is converted into calcium metaphosphate:

$$CaH_4(PO_4)_2=Ca(PO_3)_2+2H_2O.$$

The latter [or in some processes the original phosphate material] is mixed with powdered coal and sand and reduced in a continuously operated electric arc furnace, whereupon phosphorus distils over:

$$2Ca(PO_3)_2+2SiO_2+10C=2CaSiO_3+10CO+4P.$$

Before the bones are used they are subjected to various preliminary operations. In some cases the fats are first extracted (with benzine) and then treated with high-pressure steam, whereby the organic portion (the cartilaginous matter) is converted into glue. The residue consists almost wholly of calcium phosphate and carbonate, and is worked up into phosphorus as above explained.

In other instances the bones are subjected to a dry distillation, from which "DIPPEL's *animal oil*" is obtained, containing a number of important organic bases. That which remains in the retorts is *bone-black* (animal charcoal), which is used in large quantities in sugar factories to decolorize the sugar solutions. After it is no longer of use for this purpose, the animal charcoal is burned in the air, the carbon being consumed and white bone-ash remaining. This bone-ash is then sent to the phosphorus factory.

The phosphorus thus obtained is black because of adhering particles of charcoal and contains still other impurities. It can be purified by fusing it under water and pressing it through chamois; this process is usually preceded by a washing with a dilute solution of sulphuric acid and potassium dichromate, whereby the impurities are oxidized out. Finally the phosphorus is cast into sticks and in this form enters the market.

132. *Physical Properties.* — At ordinary temperatures phosphorus is a crystalline solid of a light yellow color and having a specific gravity of 1.83 at 10°. When cold it is brittle on account of its crystalline texture; above 15° it becomes soft and waxy and melts at 44.4° to a yellow, strongly refractive liquid. Its boiling-point is 290°; it then turns to a colorless vapor. In the sunlight it becomes yellow and coated with an opaque pink layer. Phosphorus is insoluble in water, slightly soluble in alcohol and ether, but easily soluble in carbon disulphide, from which it crystallizes in crystals of the regular system.

The *vapor density* of phosphorus at temperatures between 515° and 1040° is 4.58–4.50 (air = 1). Its molecular weight is therefore 123.84. Inasmuch as the smallest amount of phosphorus that is found in one gram-molecule of any of the numerous phosphorus compounds investigated is 31 g., this number therefore represents the atomic weight of the element; hence the molecule must consist of $\frac{123.84}{31} = 4$ atoms. Between 1500° and 1700° the vapor density decreases considerably, but does not quite reach the value corresponding to P_2 molecules. By the cryoscopic method also (§ 43) it has been found that the molecule of phosphorus consists of four atoms at ordinary temperatures.

133. *Allotropic Forms.*—**Ordinary,** or **yellow, phosphorus** can be transformed by heating to 250°–300° (in absence of air, necessarily) into a reddish-brown powder, **red phosphorus.** Iodine is an accelerator of this process, so that a very small quantity makes it possible for this transition to take place even below 200°. Red phosphorus is manufactured on a large scale by heating the yellow form in sealed iron cylinders for a few minutes at 250°–300°. After cooling, the product is treated with carbon disulphide and with caustic soda in order to extract the unchanged yellow phosphorus.

Red phosphorus is considerably different in its properties from the yellow form. It is not poisonous, while the latter is very much so. Red phosphorus is unaffected by the air. Its specific gravity is 2.106; it is insoluble in carbon disulphide. RETGERS has shown that it is in part crystalline. Moreover it is odorless, while yellow phosphorus gives off a peculiar odor because of the formation of ozone (§ 36). When heated in the air, it does not ignite till a temperature of 260° is reached. On the whole it is chemically much less active than yellow phosphorus.

The yellow modification can be kept for an unlimited period at ordinary temperatures; nevertheless it must be regarded as an unstable, or, rather, *metastable*, form, just like "detonating-gas," for at an elevated temperature (the higher, the faster), both pass over into more stable forms with the evolution of heat. The relative stability of the yellow phosphorus is merely a consequence of the extraordinarily small velocity with which the transformation into the red form takes place at ordinary temperatures, notwithstanding that the caloric effect of the change is considerable, viz., 32 Cal. Even at 200° molten phosphorus does not pass over into the red modification with a perceptible velocity. The presence of a catalyzer is necessary to make the velocity appreciable (§ 25). Yellow phosphorus can be regained from the red form by distilling the latter and cooling the vapor rapidly. It is a general rule that a substance which is capable of existing in different forms appears in the least stable one first. Now, if the temperature is low, the velocity of transformation of the yellow form is so small that it seems perfectly stable.

Recently still another modification has been discovered, the **scarlet phosphorus.** It is obtained by dissolving yellow phosphorus in phosphorus tribromide and boiling this solution. The new modification separates out as a very finely divided amorphous powder. The phosphorus tribromide adheres to it with great tenacity and can only be removed by boiling with water. The powder, thus purified, still contains phosphorous acid. Like red phosphorus, the scarlet form is not poisonous. It is perfectly stable in the air but reacts much more vigorously than red phosphorus. For instance, it immediately precipitates copper from a solution of copper sulphate, and with alkalies it causes a rapid evolution of PH_3, itself dissolving with the formation of hypophosphite. The scarlet phosphorus must be considered as very finely divided red phosphorus containing phosphorus tribromide or phosphorous acid in solid solution (§ 260).

134. *Chemical Properties.*—Phosphorus has a great affinity for many elements; it combines directly with all elements except nitrogen and carbon, the combination occurring with great vigor in many cases, e.g. when phosphorus is brought in contact with sulphur or bromine. Certain compounds of the metals (phosphides) are known, which are called phosphor bronzes (§ 199). Especially characteristic of phosphorus is its very strong affinity for oxygen; yellow phosphorus takes fire in the air at 40°, so that contact with a hot glass rod is sufficient to ignite it. The

burning is accompanied by a vigorous evolution of light and heat, phosphorus pentoxide, P_2O_5, being formed. On account of this strong affinity for oxygen phosphorus is a powerful reducing-agent. Sulphuric acid, when warmed with it, is reduced to sulphur dioxide; concentrated nitric acid oxidizes it with explosive violence; dilute acid evolves nitrous fumes, oxidizing the phosphorus to phosphoric acid. Many metals are precipitated by phosphorus from their salts, phosphides being formed to some extent. Silver nitrate, for instance, gives silver and silver phosphide, Ag_3P, with phosphorus; on warming phosphorus with a solution of copper sulphate copper phosphide, Cu_3P_2, is deposited.

135. The slow oxidation of phosphorus by oxygen at ordinary temperatures is accompanied by the emission of a bluish light. This *luminosity of phosphorus* is very plain in the dark.

This phenomenon is due to various circumstances, some of which are very mysterious. The oxidation, and hence the luminosity, is prevented by the presence of traces of certain substances, such as hydrocarbons, ammonia, etc. Further, the luminosity depends on the temperature; below 10° it is extremely weak. The gas pressure has a peculiar influence; at ordinary temperatures phosphorus does not emit light in pure oxygen of atmospheric pressure, but if the pressure is reduced, a point is reached at which luminosity commences; this is at 666 mm. for 15°, and at 760 mm. for 19.2°. The oxidation is therefore more vigorous in dilute oxygen (i.e. oxygen mixed with another gas, such as nitrogen) than in concentrated. VAN MARUM observed as early as 1798 that a piece of phosphorus laid on wadding (which serves as a poor conductor of heat) in a closed vessel shines the more brightly as the oxygen is pumped out, and may even take fire in very dilute gas.

The fact that oxidations are more energetic under reduced oxygen-pressure has been observed in many other cases. See § 137.

Detection of Phosphorus.—Poisonings by yellow phosphorus occur now and then. In order to detect it in such cases, use is made of its luminosity. For this purpose the contents of the stomach, which are to be tested for phosphorus, are diluted with water in a distilling-flask, connected with a condenser by a tube doubly bent at right angles. On heating the flask water distils over with a little phosphorus vapor; if the whole apparatus is placed in a dark room, a luminous ring is noticed during this distillation at the place where the steam is condensed, i.e. where the phosphorus vapor comes in contact with air in the condenser. The distillate contains phosphoric acid (MITSCHERLICH's test).

Use.—Phosphorus is used chiefly for the manufacture of matches. Matches of the old sort are prepared by dipping the ends of the sticks first in molten sulphur and then in a paste consisting of gum, an oxidizing-agent (e.g. manganese dioxide) and yellow phosphorus. By rubbing them on a rough surface enough heat is generated to set them afire. These matches are not only very poisonous on account of the yellow phosphorus they contain but also very inflammable. Moreover, their manufacture is very injurious to the health of the workmen. For this reason in some countries (e.g. in Germany and the Netherlands) their manufacture is prohibited by law. They are being gradually displaced, especially in European countries, by the Swedish safety matches, which lack this defect. In them the head consists chiefly of a mixture of potassium chlorate and antimony sulphide. They are lighted by striking them on a surface coated with some red phosphorus. To be sure, their use has the disadvantage of requiring a special ignition surface, but this on the other hand excludes the possibility of ignition by accidental friction. See also § 133.

Compounds of Phosphorus and Hydrogen.

There are three compounds of phosphorus and hydrogen known: (1) *gaseous* hydrogen phosphide, PH_3 (also called phosphine); (2) *liquid* hydrogen phosphide, P_2H_4; and (3) *solid* hydrogen phosphide, $(P_2H)_x$.

HYDROGEN PHOSPHIDE. PHOSPHINE, PH_3.

136. This compound can be prepared from the elements by bringing phosphorus together with zinc and dilute sulphuric acid, i.e. with nascent hydrogen; when thus prepared, it is mixed with a large quantity of hydrogen.

It is obtained perfectly *pure* by decomposing phosphonium iodide, PH_4I (see below); this substance, when treated with water or caustic potash, breaks up into phosphine and hydrogen iodide; the former passes off, while the latter stays in the liquid.

The generation of hydrogen phosphide by heating phosphorous and hypophosphorous acids is another example of its formation by the direct decomposition of phosphorus compounds;

$$\underset{\text{Phosphorous acid.}}{4H_3PO_3} = PH_3 + \underset{\text{Phosphoric acid.}}{3H_3PO_4}.$$

The ordinary method of preparation is by the action of phosphorus on caustic potash:

$$P_4 + 3KOH + 3H_2O = PH_3 + \underset{\text{Pot. hypophosphite.}}{3H_2KPO_2}.$$

The reaction is really more complicated than this equation indicates, for in addition hydrogen, P_2H_4 and other substances are formed. (See also § 144.)

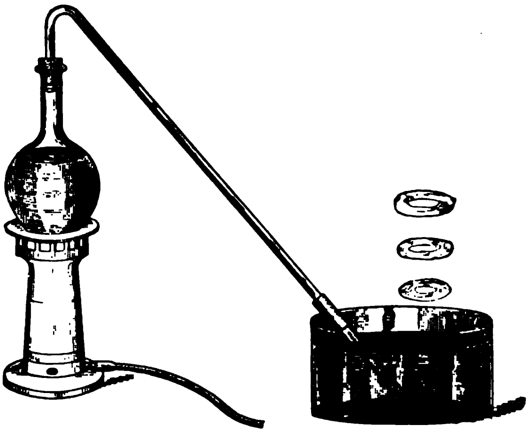


FIG. 40.—PREPARATION OF HYDROGEN PHOSPHIDE.

By reason of the presence of gaseous P_2H_4, which is self-inflammable, each bubble of gas ignites as it breakes into the air, forming usually a smoky ring of phosphorus pentoxide (Fig. 40). On account of this inflammability the vessel in which the gas is generated from phosphorus and caustic potash must be as full of liquid as possible. Moreover, the delivery-tube (preferably with a wide mouth) must open in *warm* water, in order that it may not become clogged with particles of phosphorus carried over. By passing the gas through hydrochloric acid or alcohol, the hydrogen phosphide is freed from P_2H_4 and is then no longer spontaneously combustible.

No method of producing hydrogen phosphide by the action of hydrogen on phosphorus compounds is known; however, we have one by the interaction of hydrogen compounds and phosphorus compounds. Calcium phosphide, when decomposed by water or dilute hydrochloric acid, forms hydrogen phosphide:

$$Ca_3P_2+6HCl=3CaCl_2+2PH_3.$$

The phosphides of zinc, iron, tin, and magnesium are decomposed by dilute acids with the formation of hydrogen phosphide.

Physical Properties.—Hydrogen phosphide, or phosphuretted hydrogen, PH_3, is a gas at ordinary temperatures; it becomes liquid at −85° and solid at −133.5°. It has a peculiar disagreeable odor, that reminds one of spoiled fish. It is slightly soluble in water, more so in alcohol. Sp. g. = 17 (O = 16).

137. *Chemical Properties.*—Hydrogen phosphide is very poisonous; it burns very easily, yielding phosphoric acid. In the presence of oxygen of ordinary pressure it remains unchanged; if, however, the pressure is diminished, an explosion results. This conduct reminds one of phosphorus, which is luminous (because of oxidation) only below a certain limit of pressure (§ 135).

The combustion of hydrogen phosphide may be expressed by the equation:

$$2PH_3+4O_2=P_2O_5+3H_2O.$$

Accordingly the reaction would be hexamolecular (§ 50). VAN DER STADT demonstrated by a method, similar to that referred to in § 51, that the first stage of the reaction is bimolecular and corresponds very closely to the following equation:

$$PH_3 + O_2 = H_2 + \underset{\text{Metaphosphorous acid.}}{PO_2H},$$

if the gases slowly diffuse into each other in a diluted condition.

In general, experience has taught that the mechanism of a reaction is decidedly simple and that chemical processes are almost always mono- or bimolecular. Accordingly, when the quantitative course of a reaction is represented by an equation indicating the participation of several molecules, it is probable that several intermediate reactions are involved.

Hydrogen phosphide can unite with halogen-hydrogen acids directly to form compounds of the type PH_4X (X = haolgen), in analogy with ammonia. The best known of these compounds is PH_4I, **phosphonium iodide,** a colorless, well-crystallized compound, which is formed when dry hydrogen phosphide and hydrogen iodide are mixed.

An easier method of preparation is to treat a solution of yellow phosphorus in carbon disulphide with iodine, distil off the carbon disulphide and then add water slowly, warming gently; phosphonium iodide sublimes out. The equation is

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4.$$

Phosphonium iodide is very unstable, as was mentioned in § 136; this is even more the case with phosphonium bromide, which is also a solid, but is completely dissociated into the two hydrogen compounds, PH_3 and HBr, as low as 30°. Phosphonium chloride is dissociated even at ordinary temperatures and pressures and can only exist below 14° or under more than 20 atm. pressure. Considering these properties, it is not surprising that phosphonium, PH_4,—like ammonium,—should be impossible to isolate. No other acids except those mentioned unite with hydrogen phosphide. The general behavior of the latter thus shows that it is very much less basic than ammonia.

Hydrogen phosphide possesses reducing properties. From solutions of silver nitrate or copper sulphate it precipitates a mixture of metal and phosphide; this property can be made use of to separate the gas from other gases. When mixed with chlorine it explodes vigorously, forming hydrochloric acid and phosphorus trichloride.

The *composition* of hydrogen phosphide was determined by passing a known volume over copper turnings in a heated tube. The copper combines with the phosphorus, so that the increase in weight of the tube shows the proportion of phosphorus. The escaping hydrogen is collected and measured. In the experiment it was found that hydrogen phosphide contains 91.2% phosphorus and 8.8% hydrogen. The specific gravity for $O=16$ was found to be 17; the molecular weight is therefore 34. In 34 parts there are, according to the above composition, 31 parts of phosphorus and 3 parts of hydrogen; the composition of the compound is therefore expressed by PH_3. This agrees with the results of the decomposition of hydrogen phosphide by induction sparks or by the electric arc; 1 vol. PH_3 yields $1\frac{1}{2}$ vols. hydrogen and also amorphous phosphorus, which is deposited on the sides of the tube and on the platinum wires (or carbons).

$$\underset{\text{2 vols.}}{2PH_3} = \underset{\text{3 vols.}}{3H_2} + \underset{\text{solid.}}{2P}.$$

Liquid Hydrogen Phosphide, P_2H_4.

138. In certain cases this compound is formed as a by-product in the preparation of phosphine. Especially is it formed in the decomposition of calcium phosphide with water. It also results from the oxidation of phosphine by various substances, for instance, nitrogen dioxide, by which ordinary hydrogen phosphide can be made spontaneously inflammable. The mixture of PH_3 and P_2H_4 can be separated by passing it through a well-cooled tube; the latter substance condenses to a colorless liquid, which boils at 57°-58° (under 735 mm.) and has a specific gravity of 1.01. It is easily decomposable and cannot be preserved, because it rapidly changes to the gaseous and the solid hydrogen phosphides. The same decomposition is also effected by hydrochloric acid. It must be condensed in the dark, as sunlight aids decomposition. The empirical composition is indicated by the formula PH_2; but since phosphorus is trivalent, we take P_2H_4, i.e. H_2P-PH_2, as the formula of the molecule. Liquid hydrogen phosphide thus becomes analogous to hydrazine.

Solid Hydrogen Phosphide $P_{12}H_6$.

139. This substance is formed by the decomposition of the preceding one, especially easily when phosphine charged with P_2H_4 vapor is led into concentrated hydrochloric acid. It then separates as a yellow powder of the empirical formula P_2H, whose molecular weight has been determined by cryoscopy to be $P_{12}H_6$, using yellow phosphorus as a solvent. On being heated (in a CO_2-atmosphere) it breaks up into phosphorus and hydrogen; when heated in the air it catches fire at 160°. It is insoluble in water.

Halogen Compounds of Phosphorus.

Phosphorus unites with all four of the halogens to form compounds of the types PX_3 and PX_5; the most important are the chlorides.

PHOSPHORUS TRICHLORIDE, PCl_3.

140. This compound can only be obtained by direct combination of the elements. In preparing it a rapid current of dry chlorine is led over phosphorus in a retort. The phosphorus burns with a pale yellow flame and a mixture of trichloride and pentachloride distils over into the receiver, which is kept cold. A little phosphorus is added to the distillate in order to convert the pentachloride to trichloride, and the liquid is redistilled. An easier method is to introduce phosphorus into a flask with some phosphorus trichloride and lead chlorine into the mixture.

Physical Properties.—Phosphorus trichloride is a colorless liquid of a very pungent odor; it boils at 76° and remains liquid as low as $-115°$. Sp. g. $=1.6129$ at 0°.

Chemical Properties.—Water decomposes it very rapidly with the formation of hydrochloric and phosphorous acids:

$$PCl_3+3H_2O=H_3PO_3+3HCl.$$

It is because of this decomposition that it fumes in moist air. Continued treatment with chlorine converts it into the pentachloride.

PHOSPHORUS PENTACHLORIDE, PCl_5.

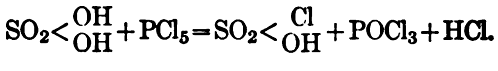
141. This substance is prepared by passing chlorine over phosphorus trichloride. Fine light-yellow crystals at once appear and the entire mass finally becomes solid, indicating that all is converted into pentachloride. This compound fumes strongly in moist air, being immediately decomposed by water with the formation of hydrochloric and phosphoric acids. When heated it sublimes without melting. In the transition to the gaseous state it breaks up at a rather low temperature into the trichloride and chlorine; this dissociation is complete at 300°, for at that point the vapor density is just half of that calculated for the pentachloride. The vapor, which at moderately low temperatures is almost colorless, takes on the yellow color of chlorine for the above reason, as the temperature rises. The dissociation products, phosphorus trichloride and chlorine can be separated by diffusion. Phosphorus pentachloride evaporates in an atmosphere of the trichloride with almost no dissociation (*cf.* § 51).

By the addition of a little water it is converted into phosphorus oxychloride:

$$PCl_5+H_2O=POCl_3+2HCl.$$

With more water phosphoric and hydrochloric acids are produced.

Phosphorus pentachloride is used in organic chemistry to replace hydroxyl groups with chlorine. In inorganic chemistry, it can also be employed for the same purpose; thus sulphuric acid reacts with it in the following manner (§ 93):



$$SO_2<{OH \atop OH}+PCl_5=SO_2<{Cl \atop OH}+POCl_3+HCl.$$

PHOSPHORUS OXYCHLORIDE, $POCl_3$.

142. The best method of preparing this compound is by the oxidation of the trichloride with sodium chlorate:

$$3PCl_3+NaClO_3=3POCl_3+NaCl.$$

In order to moderate the great vigor of this reaction sodium chlorate is placed under phosphorus oxychloride and the trichloride is then added slowly by means of a dropping-funnel.

Phosphorus oxychloride is a colorless, mobile liquid, that boils at 107.2° and, when solid, melts at −1.5°. Sp. g. =1.7118 at 0°. In the presence of water, with which it is not miscible, it slowly changes to phosphoric and hydrochloric acids:

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

THE COMPOUNDS OF PHOSPHORUS WITH THE OTHER HALOGENS.

143. These are very analogous to the chlorine derivatives. They are likewise prepared by direct synthesis from the elements. Inasmuch as the reaction is very vigorous, it has to be moderated by dissolving the phosphorus and the halogen separately in carbon disulphide, slowly adding one to the other and then distilling off the solvent. The fluorides have special methods of preparation. All these compounds are broken up by water like the corresponding chlorides, the fluorides, however, quite slowly.

The *composition of these compounds* can be ascertained in the following way: on being decomposed by water they yield phosphoric or phosphorous acid and a halogen acid, so that the quantities of phosphorus and halogen present can be found by determining the amounts of these acids. Moreover, the molecular weight can be obtained by measuring the vapor density, though it must be borne in mind, however, that compounds of the type PX_5 are usually dissociated in the gaseous state.

Oxygen Compounds of Phosphorus.

144. Three compounds of this class are known: *phosphorus trioxide*, P_2O_3; *phosphorus tetroxide*, P_2O_4; and *phosphorus pentoxide*, or *phosphoric anhydride*, P_2O_5. Only the last is of any great importance.

Phosphorus Trioxide, P_2O_3.

This compound is produced when phosphorus burns in a slow current of dry air in a tube. The principal product is phosphorus pentoxide, which can be collected by a wad of glass fibers. The phosphorus trioxide passes through as a vapor and is condensed in a well-cooled tube. It is a white waxy substance when thus formed, but it can also be obtained in crystals; the latter melt at 22.5° and boil at 173.1° (in a nitrogen atmosphere). The vapor density has been found to be 109.7, while that calculated for P_4O_6 is 110. On being heated to 440° it is decomposed into red phosphorus and phosphorus tetroxide. It turns yellow in the light, which explains the fact that phosphorus pentoxide sometimes takes on a yellow color. It dissolves slowly in cold water forming phosphorous acid; with hot water it produces red phosphorus, self-inflammable hydrogen phosphide and phosphoric acid in a vigorous reaction. When heated to 50°–60° in the air it takes fire and burns to the pentoxide.

Phosphorus Tetroxide, P_2O_4,

is obtained from the P_2O_3 compound, as was stated above. It forms colorless glistening crystals, that break up in water into phosphorous and phosphoric acids. In this respect its conduct is analogous to that of nitrogen tetroxide, which yields nitrous and nitric acids with water.

PHOSPHORUS PENTOXIDE, P_2O_5.

This compound is the product of the combustion of phosphorus in oxygen or an excess of dry air. It forms a white, voluminous, snow-like mass, that takes up water rapidly to produce phosphoric acid. It is the most powerful desiccating-agent known. MORLEY ascertained that it dries the air down to 1 mg. water vapor in 40,000 l. air. It exists in two modifications, both of which are formed simultaneously in the above process. The one is crystalline, subliming at 250°; the other amorphous and not volatile below red heat; the vapor condenses crystalline. When heated above 250° the crystalline modification passes over into the amorphous form.

Heating with charcoal reduces it to phosphorus.

The vapor density of phosphoric anhydride at bright redness was found to correspond to the formula $(P_2O_5)_2$.

Acids of Phosphorus.

145. Only two of the above described oxides of phosphorus, viz. P_2O_3 and P_2O_5, form corresponding acids; these oxides can unite with different amounts of water to form acids. From P_2O_5 we have:

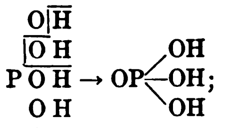
$P_2O_5 + H_2O = 2HPO_3$, *metaphosphoric acid,*
$P_2O_5 + 2H_2O = H_4P_2O_7$, *pyrophosphoric acid,* and
$P_2O_5 + 3H_2O = 2H_3PO_4$, *orthophosphoric acid.*

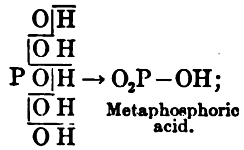
From the other oxide two acids can be derived: *metaphosphorous acid,* HPO_2, and *phosphorous acid,* H_3PO_3. Besides these there are two acids of phosphorus, whose anhydrides are unknown, viz. *hypophosphorous acid,* H_3PO_2, and *hypophosphoric acid,* $H_4P_2O_6$.

The relation between ortho-, meta-, and pyrophosphoric acids can be shown in another way, which leads us to make some general observations. It was remarked in § 141 that phosphorus pentachloride is transformed by water into phosphoric and hydrochloric acids. The action of water on the pentachloride may be regarded as consisting first of a substitution of all five chlorine atoms by hydroxyl:

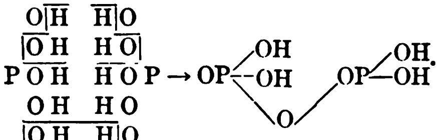
$$P\boxed{Cl_5 + 5H}OH = 5HCl + P(OH)_5.$$

This compound, which would strictly be regarded as orthophosphoric acid, is unknown; a molecule of water is at once split off, forming the ordinary phosphoric acid, H_3PO_4, which we are accustomed to call orthophosphoric acid. In a similar way the metaphosphoric acid can be derived from the acid $P(OH)_5$ by the splitting off of two molecules of water:


Orthophosphoric acid.


Metaphosphoric acid.

while the pyrophosphoric acid can be regarded as $2P(OH)_5 - 3H_2O$:


Pyrophosphoric acid.

Orthophosphoric acid can also be derived from phosphorus oxychloride:

$$OP\boxed{Cl_3 + 3H}OH \rightarrow OP(OH)_3.$$

This way of looking at them makes plain not only the connection between the different acids, but also their structural formulæ. The same method can be applied to many other cases. As an example we may select the *per-iodic acids*. In § 62 only one was mentioned. There are salts, however, of various per-iodic acids, e.g. MIO_4, M_3IO_5, M_5IO_6, etc. These can be derived from a hypothetical acid $I(OH)_7$ in which iodine is joined to as many hydroxyls as correspond to its maximum valence. M_5IO_6 would come from $I(OH)_7-1H_2O$; M_3IO_5 from $I(OH)_7-2H_2O$; and MIO_4 from $I(OH)_7-3H_2O$.

ORTHOPHOSPHORIC ACID, H_3PO_4.

146. This acid can be obtained by direct synthesis from its elements; phosphorus burns to the pentoxide and the latter yields the acid on dissolving in water. Its formation by the action of nitric acid on phosphorus was mentioned in § 134. It can also be obtained by the oxidation of compounds containing phosphorus and hydrogen; phosphine and the lower acids of phosphorus are oxidized to phosphoric acid.

Ordinarily this acid is prepared by the oxidation of phosphorus with nitric acid or by liberating it from its salts, particularly the calcium salt, $Ca_3(PO_4)_2$. The latter is stirred into the theoretical amount of dilute sulphuric acid, forming calcium sulphate, which is only slightly soluble in water, and phosphoric acid, which goes into solution. On evaporating this solution the acid remains.

At ordinary temperatures orthophosphoric acid is a crystalline solid. It melts at 38.6°, is odorless and extremely soluble in water, forming a strongly acid solution.

It has the character of a strong acid; however, it is considerably less ionized than hydrochloric acid; a solution of 1 mole phosphoric acid in 10 l. water contains about one-fourth as many hydrogen ions as hydrochloric acid of the same molecular concentration. It is ionized chiefly into $H^{\cdot}$ and H_2PO_4'. It generates hydrogen with metals, all three hydrogen atoms being replaceable by metallic atoms; it is therefore **tribasic.** Three classes of salts are possible and known to exist; these are the **primary, secondary** and **tertiary** salts. Of the alkali salts all three kinds are soluble; of the alkaline earth salts only the primary, the tertiary and secondary being insoluble. The other phosphates are insoluble in water but are dissolved by mineral acids.

This latter property is due to the fact that phosphoric acid is a weaker acid than the strong mineral acids, hydrochloric, nitric and sulphuric. On treating an insoluble phosphate with one of these acids, e.g. hydrochloric, undissociated molecules of phosphoric acid are formed in the liquid; the more hydrochloric acid, the more the association, since the hydrochloric acid reduces the ionization of phosphoric acid. H_2PO_4' and $H^\cdot$ ions thus disappear and, in case enough hydrochloric acid is added, the concentration of the H_2PO_4' ions remaining will not be great enough together with that of the metal ions present to reach the value of the solubility product; hence all the phosphate must dissolve (§ 73).

For the same reason, *as a general rule, salts that are insoluble in water will only dissolve in acids that are stronger than the acid of the salt.* The only exception to this is the case when the value of the solubility product of the insoluble salt is very small, examples of which we have seen in certain sulphides (§ 73).

When heated to 213° orthophosphoric acid gives off water, forming mainly the pyro-acid but also a little meta-acid throughout the reaction. The pyro-acid on the other hand is converted by further heating into the meta-acid.

With silver nitrate orthophosphates give a yellow precipitate of silver phosphate, Ag_3PO_4, soluble in nitric acid and ammonia. In the case of a primary or secondary phosphate, the precipitation is not complete, since nitric acid is liberated in the reaction:

$$Na_2HPO_4+3AgNO_3=Ag_3PO_4+2NaNO_3+HNO_3,$$

or, expressed in ions:

$$HPO_4''+3Ag^\cdot \rightleftarrows Ag_3PO_4+H^\cdot.$$

If, however, an excess of sodium acetate is added, the precipitation is practically complete.

The reason for this is obvious. By the addition of acetate the acetic anions $C_2H_3O_2'$ are forced to combine with the $H^\cdot$ ions, for acetic acid is only very slightly ionized and its ionization is, moreover, considerably lessened by the excess of sodium acetate. The result is that in the equilibrium $HPO_4''+3Ag^\cdot \rightleftarrows Ag_3PO_4+H^\cdot$ the $H^\cdot$ ions are removed. The inverse reaction ← is then no longer possible, and the direct reaction → must therefore become complete, or in other words, all the phosphoric acid is precipitated as silver phosphate.

It was stated above that the alkali salts of phosphoric acid are soluble in water. These aqueous solutions differ markedly in reaction. The solution of a primary salt, KH_2PO_4, is acid, that of a secondary salt feebly alkaline, and that of a tertiary salt strongly alkaline. The cause of this variation must be more fully explained.

The acid reaction of a salt such as KH_2PO_4 must be attributed to the fact that its anion, H_2PO_4' (analogous to the anion HSO_4'), is capable of splitting up into the ions $H^{\cdot}$ and HPO_4'', the former producing the acid reaction. The feebly alkaline reaction of a salt like K_2HPO_4 is accounted for by hydrolysis (§ 66). Such a salt is extensively ionized in dilute solution into $2K^{\cdot}$ and HPO_4''. However, while H_3PO_4 is rather highly dissociated (into $H^{\cdot}$ and H_2PO_4'), H_2PO_4' is but slightly ionized into $H^{\cdot}$ and HPO_4''. In this case H_2PO_4' behaves as a weak acid. Hence, if there is a large proportion of HPO_4'' ions in a solution, they will tend to unite with $H^{\cdot}$ ions, because the system $H^{\cdot}+HPO_4'' \rightleftarrows H_2PO_4'$ is only in equilibrium when the right-hand side preponderates. The necessary $H^{\cdot}$ ions are supplied by the water, which is split up to a very slight extent into $H^{\cdot}$ and OH'. But when the $H^{\cdot}$ ions unite with HPO_4'' ions we have a surplus of OH' ions in the solution and the latter takes on an alkaline reaction. Entirely analogous is the explanation of the strongly alkaline reaction of the tertiary phosphates, such as K_3PO_4. Their aqueous solutions contain the ions PO_4''', which have a still stronger tendency to unite with $H^{\cdot}$ ions than the HPO_4'' ions. The PO_4''' ion, therefore, causes the presence of an even larger proportion of OH' ions, not compensated by $H^{\cdot}$ ions, so that the result is a strongly alkaline reaction.

Phosphoric acid is precipitated from an ammoniacal solution by a magnesium salt as white crystalline *ammonium magnesium phosphate*, $NH_4MgPO_4+6H_2O$. Another very characteristic test for phosphoric acid is that in nitric acid solution a finely crystalline, yellow precipitate is produced by ammonium molybdate, especially on warming. This precipitate has approximately the composition $14MoO_3+(NH_4)_3PO_4+4H_2O$, i.e. it is an ammonium phospho-molybdate. Precipitation in acid solution is of great advantage here, since most of the phosphates are soluble only in acids.

PYROPHOSPHORIC ACID, $H_4P_2O_7$.

147. One method of producing this acid was given in the preceding paragraph. In preparing it, it is more practicable, however, to heat the secondary sodium phosphate (the ordinary sodium phosphate of commerce), because in this case only one molecule of water can be driven off from two molecules of the salt:

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

After being heated the sodium pyrophosphate is dissolved in water and lead acetate is added to precipitate lead pyrophosphate, which is then decomposed with hydrogen sulphide.

Pyrophosphoric acid can be obtained from its solution as a colorless vitreous mass by evaporation in a vacuum at a low temperature. When dissolved in water of ordinary temperature, the acid remains unchanged for quite a while; on warming this solution, especially after the addition of a little mineral acid, it is converted into ortho-acid (§ 145).

All four hydrogen atoms are replaceable by metals; we should therefore expect to find four classes of salts. In reality only two are known, $M_4P_2O_7$ and $M_2H_2P_2O_7$. The neutral, as well as the acid, salts of the alkalies are soluble in water; the neutral salts of other bases are insoluble, the acid salts chiefly soluble.

Pyrophosphoric acid is distinguished from the ortho-acid by the fact that solutions of its salts give a *white* precipitate, $Ag_4P_2O_7$, with silver nitrate, and from the meta-acid by not coagulating albumen and giving no precipitate with barium chloride.

METAPHOSPHORIC ACID, HPO_3.

148. This acid is obtained by heating the ortho- or the pyro-acid till no more water passes off, or by heating ammonium phosphate $(NH_4)_2HPO_4$. Moreover, on dissolving phosphorus pentoxide in cold water, the product is at first chiefly meta-acid.

At ordinary temperatures metaphosphoric acid is a vitreous solid (hence the name *glacial phosphoric acid*), which can be melted and easily drawn out into threads. On being heated strongly it volatilizes without breaking up into water and pentoxide. When boiled in aqueous solution it goes over into orthophosphoric acid. It is very deliquescent; use is made of this property occasionally.

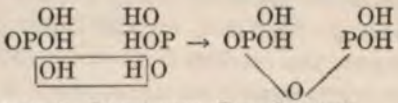
Metaphosphoric acid is monobasic, corresponding to the formula HPO_3. Its alkali salts only are soluble in water. In solution the meta-acid can be distinguished from the ortho- and the pyro-acids by its ability to coagulate albumen and give white precipitates with chlorides of barium or calcium.

The vapor of this substance at bright-red heat consists chiefly of $H_2P_2O_6$ molecules (di-metaphosphoric acid), which are apparently liable to undergo partial dissociation and even to lose a small quantity of water.

There are salts of various acids known, which must be regarded as polymers of metaphosphoric acid, e.g. $K_2P_2O_6$, potassium di-metaphosphate; there exist also tri-, tetra-, and hexa-metaphosphates, i.e. salts of the acids $H_3P_3O_9$, $H_4P_4O_{12}$, and $H_6P_6O_{18}$.

Hypophosphoric Acid, $H_4P_2O_6$.

149. When sticks of phosphorus are suspended in a solution of sodium acetate in such a way that only 0.5 cm. is exposed above the level of the liquid and the temperature is kept between 6° and 8°, the phosphorus oxidizes slowly and the difficultly soluble acid sodium salt of hypophosphoric acid, $Na_2H_2P_2O_6 + 6H_2O$ soon begins to crystallize out. It can be purified by crystallization from a dilute solution of acetic acid. If this salt is dissolved in water and barium chloride added, a precipitate of barium hypophosphate is formed, from which an aqueous solution of the free acid can be obtained by means of dilute sulphuric acid. This can be evaporated at 30° to a sirupy consistency without decomposition and, when left in a vacuum, yields crystals of the acid. At an elevated temperature and in the presence of a mineral acid phosphorous and phosphoric acids are formed. This behavior justifies the consideration of hypophosphoric acid as a mixed anhydride of the two last-named acids:



Phosphoric acid. Phosphorous acid. Hypophosphoric acid.

However, it has not yet been possible to prepare the hypophosphoric acid by melting together the other two acids.

From the determination of the molecular weight of the methyl ester it seems probable that the formula of the acid is H_2PO_3 and not $H_4P_2O_6$

Metaphosphorous Acid, HPO_2.

150. This compound was discovered by VAN DER STADT during the slow oxidation of phosphine under reduced pressure (§ 137):

$$PH_3 + O_2 = H_2 + HPO_2.$$

The sides of the vessel become covered with feather-like crystals of HPO_2. These melt at a much higher temperature than the crystals of phosphorous acid and are converted into the latter by the action of water vapor.

PHOSPHOROUS ACID, H_3PO_3.

151. In § 149 it was mentioned that this acid is formed by the slow oxidation of phosphorus in moist air. It is more easily prepared by decomposing phosphorus trichloride with water:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The hydrochloric acid can be expelled by evaporating at 180° and the phosphorous acid crystallizes out on cooling.

The melting-point of phosphorous acid is 70.1°. It is a very hygroscopic substance Heating decomposes it into phosphoric acid and phosphine. It has a strong reducing action, being itself oxidized to phosphoric acid. The oxygen of the air acts on it very slowly. It precipitates the metals from solutions of gold chloride, mercuric chloride, silver nitrate, etc. A characteristic reaction is the reduction of sulphur dioxide to sulphur, which takes place at ordinary temperatures, when solutions of the two substances are mixed.

In spite of its *three* hydrogen atoms, phosphorous acid acts as a *dibasic* acid. As we have already observed, the ionization of polybasic acids sometimes affects only one $H^{\cdot}$ ion at first, the others being split off with increasing difficulty. According to OSTWALD it may be supposed that ionization beyond $2H^{\cdot}$ and HPO_3'' is in this case so difficult that the acid seems to be only dibasic. The phosphites are not oxidized by the air, but they yield to the action of oxidizing-agents; e.g. they liberate the precious metals from their salts, as does also the acid itself. Heating breaks them up into hydrogen, pyrophosphates and phosphide. The double phosphites give precipitates with baryta- or lime-water.

Hypophosphorous Acid, H_3PO_2.

152. Salts of this acid are produced by heating phosphorus with caustic soda, lime-water or baryta-water (§ 136):

$$3Ba(OH)_2 + 8P + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3.$$

It can be set free from these salts by sulphuric acid; the aqueous solution is concentrated at 80°–90° and then cooled strongly, whereupon the acid crystallizes out. Melting-point, 26.5°. On being heated at 130°–140° the acid splits up into phosphorous acid and phosphine; at a somewhat higher temperature the latter acid yields phosphine and phosphoric acid. The equations are:

$$3H_3PO_2 = 2H_3PO_3 + PH_3; \quad 3H_3PO_3 = 2H_3PO_4 + PH_3.$$

Hypophosphorous acid is a very strong reducing-agent. Gold, silver and mercury are precipitated from solutions of their salts by the free acid as well as its salts. Sulphur dioxide is reduced to sulphur at ordinary temperatures. In these reactions the acid itself is converted into phosphoric acid. It is distinguished from phosphorous acid by its behavior towards copper sulphate solution; when it is warmed with the latter, a red precipitate of copper hydride, Cu_2H_2, is formed. Hypophosphorous acid is monobasic.

Compounds of Phosphorus and Sulphur.

153. Various compounds of this sort are known; all of them are obtained by warming the two elements together. As the reaction is very vigorous with yellow phosphorus, the red form is usually employed.

The compound P_2S_5, which is of service in organic chemistry, is a yellow crystalline substance, melting at 274°–276° and boiling at 518°. On being warmed with water it yields phosphoric acid and sulphuretted hydrogen. P_2S_5 unites with 3 molecules of K_2S to form a *sulphophosphate*, K_3PS_4, i.e. a phosphate whose oxygen is replaced by sulphur.

Several compounds containing a halogen in addition to phosphorus and sulphur are known, e.g. $PSCl_3$. This *phosphorus sulphochloride* can be prepared by treating phosphorus pentachloride with hydrogen sulphide, a method analogous to that of forming the oxychloride from the pentachloride and water. A more convenient method is by the action of the pentachloride on the pentasulphide, which carries out the analogy, to oxy-compounds still farther (§ 142):

$$3PCl_5 + P_2S_5 = 5PSCl_3.$$

It is a colorless liquid, boiling at 125°. Water decomposes it into phosphoric acid, hydrochloric acid and hydrogen sulphide.

Compounds containing Phosphorus and Nitrogen.

154. The compounds of this class are also numerous. Among them are *amidophosphoric acid*, $OP^{(OH)_2}_{NH_2}$, and *diamidophosphoric acid*, $OP^{OH}_{(NH_2)_2}$. As their names indicate, these compounds behave like acids.

If dry ammonia is conducted over phosphorus pentachloride, a white mass is obtained which consists supposedly of ammonium chloride, NH_4Cl, and a compound $PCl_3(NH_2)_2$. With water it forms *phosphamide*, $PO(NH)(NH_2)$, a white insoluble powder. On being boiled with water secondary ammonium phosphate is formed:

$$PO(NH)(NH_2) + 3H_2O = OP^{OH}_{(ONH_4)_2}$$

The name *phospham* is given to a compound $P_3H_3N_6$, which is formed from the product of the action of ammonia on phosphorus pentachloride, when it is heated in the absence of air till no more ammonium chloride fumes appear. It is insoluble in water. When fused with potassium hydroxide, it breaks up as follows:

$$P_3H_3N_6 + 9KOH + 3H_2O = 3K_3PO_4 + 6NH_3.$$

ARSENIC.

155. Arsenic occurs in nature in the free state—native. More frequently it is found in combination with sulphur (*realgar*, As_2S_2, and *orpiment*, As_2S_3) and with metals (*arsenopyrite*, or *mispickel*, $FeAsS$, and *cobaltite*, $CoAsS$); also with oxygen as As_2O_3 (*arsenolite*).

The extraction of the element from these minerals is simple.

Arsenopyrite yields arsenic on mere heating, the latter subliming. Arsenolite is reduced with carbon:

$$2As_2O_3+6C=As+6CO.$$

Physical Properties and Allotropic Conditions.—The condition in which arsenic usually occurs is the crystalline. It then has a steel-gray color and a specific gravity of 5.727 at 14° and is a good conductor of electricity. It sublimes under ordinary pressure without melting; under increased pressure, however, it melts at 500°. By sublimation in a current of hydrogen a second crystallized form can be obtained together with a black modification, which according to RETGERS is also crystallized. An amorphous modification results from the decomposition of hydrogen arsenide by heat, the arsenic appearing as a dark brown deposit on the sides of the glass. Finally there is a yellow modification which is formed when arsenic vapor is condensed in a dark room by liquid air. This yellow arsenic is very sensitive to light; even at the temperature of liquid air ($-180°$)—at which it is stable in the dark—it is converted into the black modification by the light of a Welsbach burner. It is a remarkable fact that a solution of the yellow modification in chlorine is much more stable toward light and heat than is the pure substance. Such solutions are obtained in concentrations up to 7%; when they are cooled yellow arsenic crystallizes out. The relation between yellow and black arsenic is very analogous to that between yellow and red phosphorus, except that in the case of arsenic the yellow form is much less stable. At an elevated temperature (360°) all the modifications pass over into the ordinary crystalline form.

Vapor Density.—The lemon-yellow vapor of arsenic has a density of 10.2 (air=1) at about 860°, which makes the molecular weight 293.8. At 1600°–1700° the vapor density is less by half, being 5.40. Since the atomic weight of arsenic is 75, its molecule therefore contains four atoms at about 860° and two at 1600°–1700°.

Chemical Properties.—Arsenic is not affected by dry air at ordinary temperatures; in moist air it becomes covered with a coating of oxide. At 180° it burns with a bluish flame to the oxide As_4O_6, giving off a peculiar garlic-like odor. At an elevated temperature it combines with many elements directly; it unites with chlorine without the aid of heat, producing scintillations.

HYDROGEN ARSENIDE. ARSINE, AsH_3.

156. Direct synthesis from the elements is not possible with this compound. It is formed when almost any arsenic compound comes in contact with nascent hydrogen (zinc+sulphuric acid). When thus prepared it contains considerable hydrogen, however. Pure arsine is obtained by treating zinc arsenide or sodium arsenide with dilute sulphuric acid:

$$As_2Zn_3+3H_2SO_4=2AsH_3+3ZnSO_4.$$

Physical Properties.—Hydrogen arsenide is a gas; it liquefies at −40°, but does not solidify as low as −110°. Sp. g.=38.9 (H=1). It must be handled with great care, as it is very poisonous. Fortunately its presence can be easily detected by its peculiar, disagreeable odor.

Chemical Properties.—Arsine can be decomposed into its elements by heat. If the gas is passed through a hot glass tube, arsenic is deposited on the sides in the form of a metallic mirror. Induction sparks also decompose it. By the latter means it can be shown that the resulting volume of hydrogen is 1½ times as large as that of the gas itself, in accord with the formula AsH_3. It is an endothermic compound,

$$As+3H-AsH_3=-36.7 \text{ Cal.},$$

and has been made to explode by fulminating mercury (§ 119).

Hydrogen arsenide burns with a pale flame, yielding water and arsenious oxide, As_2O_3, if sufficient air is present; if such is not the case, or if the flame is cooled, arsenic is deposited. On heating potassium or sodium in the gas, an arsenide, AsK_3 or $AsNa_3$, is formed. Hydrogen arsenide precipitates the yellow compound $AsAg_3 \cdot 3AgNO_3$ from a very concentrated solution of silver nitrate:

$$AsH_3+6AgNO_3=AsAg_3 \cdot 3AgNO_3.$$

This is decomposed by the addition of water into arsenious acid, nitric acid and metallic silver, the latter being deposited.

This reaction is called GUTZEIT'S *test*. It is usually carried out in the following way: A drop of 50% $AgNO_3$ solution is placed on a piece of filter paper and the moist spot is held over a test-tube containing some zinc, dilute sulphuric acid and the substance to be tested for arsenic. A plug of cotton is inserted near the top to protect the paper from being spattered by the effervescing solution. If arsenic is present, the spot becomes yellow, and turns black when moistened with water.

Composition of Arsine.—If arsine is passed over hot copper oxide, water and copper arsenide are formed. The ratio of hydrogen to arsenic in arsine is determined from this reaction. For 1 part (by weight) of hydrogen 24.97 parts of arsenic are obtained. The molecular weight of the compound, as found from the specific gravity (see above), is 77.9; since the atomic weight of arsenic is 75, the formula of arsine must be AsH_3.

Detection of Arsenic.

157. The majority of arsenic compounds are very poisonous. Several of them are of practical use and hence are on the market, e.g. white arsenic, As_2O_3 (rat-poison); orpiment, As_2S_3; Schweinfurt green, or copper arsenite. Poisonings with these substances happen occasionally. Some arsenic compounds, because of their pretty green color, are still used, though much less than formerly, in dyeing tapestries, portières, and the like. Rooms in which these are hung usually contain particles of arsenical matter, which are injurious to the health. Further, a certain species of mould, *penicillium brevicaule*, which is sometimes found in such tapestries, has the power of generating volatile and very poisonous arsenic compounds. The chemist is therefore quite frequently called upon to analyze a given sample (of dyed materials or the like, or the contents of a stomach) for arsenic. For this purpose a method has been devised which enables him to detect with certainty extremely small amounts of arsenic. It involves the following operations: The organic substance in question is at first disintegrated as well as possible, usually by digestion with hydrochloric acid on the water bath, a little potassium chlorate being added from time to time. Thus the arsenic compound is oxidized to arsenic acid. When the chlorine has been expelled by warming and the liquid has been filtered, hydrogen sulphide is passed in for some time at a temperature of about 80° to precipitate the arsenic as sulphide. The sulphide is then dissolved in nitric acid (in case the presence of antimony is suspected it must first be removed); this solution is evaporated to dryness to get rid of the excess of acid, the dry residue is dissolved in water, and this

liquid is then tested in the **Marsh** apparatus, a simple form of which is shown in Fig. 41.

This consists of a small flask, in which hydrogen is generated from zinc and sulphuric acid; the liquid to be investigated is poured down the thistle-tube; if arsenic is present, arsine is formed. The mixture of hydrogen and arsine is dried by calcium chloride in the wide tube and then enters a tube of hard glass, which is narrowed at several places and drawn to a point at the further end. As the gas leaves the tapering end, which is bent upward, it is lighted. Thereupon the tube is heated with a flame on the near side of a narrowed place. The arsine is broken up and arsenic is deposited as a bright metallic mirror in the narrowed part. From the extent and thickness of the deposit one can estimate the number of milligrams of arsenic present. If the hydrogen arsenide is not heated, it passes on to the flame and is burned. A cold porcelain dish held in the flame is soon coated with a deposit of arsenic, which is readily soluble in sodium hypochlorite solution (sodium arsenate being formed). This solubility enables us to distinguish arsenic from antimony.

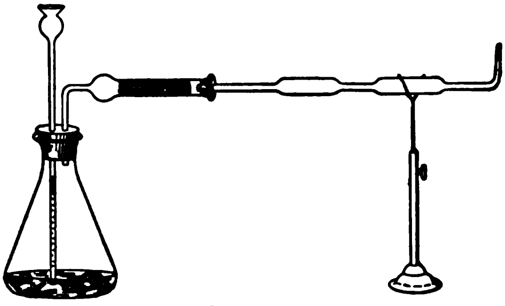


Fig. 41.—Marsh Apparatus.

Arsenic is very widely distributed, although in small amounts; hence we always have to reckon with the possiblity of traces of it being present in the reagents and glass utensils of the laboratory. In order to test this a "blank experiment" is performed, i.e. all the operations are carried out with duplicate amounts of the required chemicals but without the addition of the substance to be analyzed. Not until the materials used are proved to be free from arsenic is it permissible to use them in an actual test.

Whether or not textile fabrics and the like have been dyed with Schweinfurt green (copper arsenite) can be determined easily by the **Gutzeit** test. Another method is to use the above-mentioned *penicillium brevicaule.* This is cultivated on bread which is soaked with the liquid to be tested for arsenic. The least trace of the latter reveals itself by a characteristic garlic-like odor, caused by the evolution of arsenical gases.

Compounds of Arsenic with the Halogens.

158. Three arsenic-halogen compounds of the type AsX_5 are known; viz., the pentachloride, $AsCl_5$, the penta-iodide, AsI_5, and the pentafluoride, AsF_5. Aside from these only compounds of the type AsX_3 are known.

Arsenic trichloride, $AsCl_3$, can be obtained by direct synthesis or by the action of hydrochloric acid on white arsenic. The latter way is analogous to the formation of metal chlorides from the oxide and hydrochloric acid. This compound is a colorless oily liquid having a specific gravity of 2.205 (d_4^0). It freezes at $-18°$ and boils at 130.2°. It is extremely poisonous. When exposed to the air it throws off dense white fumes. With a little water it forms an oxychloride, $As(OH)_2Cl$; with much water hydrochloric acid and arsenious oxide. In this latter system a rise of temperature results in partial re-formation of the trichloride, which is volatile with the water vapor. The following equilibrium seems to exist:

$$As_2O_3 + 6HCl \rightleftarrows 2AsCl_3 + 3H_2O.$$

Oxygen Compounds of Arsenic.

Two such compounds are known: As_2O_3, *arsenious oxide,* and As_2O_5, *arsenic oxide.*

ARSENIOUS OXIDE, As_2O_3.

159. Arsenious anhydride (commonly called "arsenic" or "white arsenic") is found in nature. It is formed by the combustion of arsenic in air or oxygen and by the oxidation of arsenic with dilute nitric acid. It is manufactured commercially by roasting arsenical ores; the oxide volatilizes and is condensed in brick-walled chambers, where it collects as a white powder ("arsenic meal") .It is refined by sublimation from iron cylinders.

Physical Properties.—Arsenious oxide is an odorless solid, that does not melt under ordinary pressure, but sublimes. Under higher pressure it is possible to melt it. At 800° its vapor density is 198 (O = 16), which makes the molecular formula As_4O_6. Above this temperature dissociation begins and at 1800° the vapor density corresponds to the formula As_2O_3. By the ebullioscopic method (elevation of the boiling-point) the molecular formula has been found to be As_4O_6 at 205° also (in boiling nitrobenzene).

Various Modifications.—Arsenious oxide is known in a vitreous form as well as in crystals of the regular and monoclinic systems.

The vitreous modification is produced when the compound is sublimed or heated to the sublimation-point. Sp. g. = 3.738. After standing for some time at ordinary temperatures, this form becomes white like porcelain because of conversion into isometric crystals. The latter form is better obtained by dissolving the vitreous modification in water or hydrochloric acid and letting it crystallize out. During the crystallization the strange phenomenon of bright luminescence is observed, which is caused by the breaking of the crystals. This phenomenon, which is also noticed in other crystallizations, is called triboluminescence. The transformation of the amorphous into the regular variety is accompanied by the evolution of heat (5.330 Cal.). The monoclinic form is obtained by conducting the crystallization above 200° instead of at ordinary temperatures. If the lower half of a sealed glass tube containing arsenious oxide be heated above 400°, it will be found after cooling that the lower heated part contains vitreous, the middle monoclinic, and the upper octahedral, arsenious oxide.

Since the transformation of amorphous into crystallized arsenious oxide takes place even at ordinary temperatures (rapidly at 100°) and with the evolution of heat, the octahedral form is to be regarded as the stable one at ordinary temperatures; the glassy form is only able to exist at these temperatures, because the velocity of transformation is then very small. According to the above, if octahedral arsenious oxide is gradually warmed, we have first a transformation into monoclinic and then another into amorphous arsenious oxide. The transition temperatures have not yet been determined.

Chemical Properties.—Arsenious oxide is easily reduced to arsenic; for example, by heating with charcoal or nascent hydrogen. It is also easily oxidized to arsenic oxide and is therefore useful as a reducing-agent. This oxidation can be brought about by chlorine, bromine (bromine-water), iodine solution, potassium permanganate, strong nitric acid, etc. It is slightly soluble in water; the solution has a salty metallic taste and a weak acid reaction. In acids it dissolves much more easily, because it acts towards them as a basic oxide. It was stated above (§ 158) that a solution of the oxide in hydrochloric acid gives off arsenious chloride. White arsenic is a rank poison; freshly precipitated ferric hydroxide serves as an antidote.

ARSENIC OXIDE, $(As_2O_5)_x$.

160. This compound cannot be prepared like the corresponding phosphorus compound by burning arsenic in the air, for the oxidation goes no farther than to arsenious oxide. The higher oxide can only be prepared by heating arsenic acid in the air:

$$2H_3AsO_4 - 3H_2O = As_2O_5.$$

This arsenic anhydride is a white glassy substance, that dissolves in water slowly, going over into arsenic acid. By heating with carbon it is easily reduced to arsenic. At an elevated temperature it breaks up into oxygen and arsenious oxide. Its molecular weight is not known; the formula As_2O_5 is simply empirical.

Oxyacids of Arsenic.

Two of these are known: *arsenious acid,* H_3AsO_3 (only in aqueous solution and salts) and *arsenic acid,* H_3AsO_4.

ARSENIOUS ACID, H_3AsO_3.

161. This acid exists in the aqueous solution of the anhydride. It still remains to be discovered, however, which hydrate, H_3AsO_3, $HAsO_2$ or some other, is present. On evaporation the anhydride and not the acid separates out. This acid forms three classes of salts, according as one, two, or three of its hydrogen atoms are replaced by metals; it is therefore tribasic. Certain salts are known which are derived from a *meta-arsenious acid,* $HAsO_2$.

The salts of the alkalies are soluble in water; those of the other metals are not, but dissolve easily in acids, however. A neutral arsenite- solution gives a yellow precipitate of silver arsenite, Ag_3AsO_3, with silver nitrate.

The solution of the free acid is easily oxidized to arsenic acid by iodine solution:

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI.$$

Such a solution can therefore also be employed for the titration of iodine (§ 93).

COUPLED, OR INDUCED, REACTIONS.

When one substance is being oxidized by another it is often found that, if arsenious acid is added to the mixture, this latter substance is also oxidized, even though it be not attacked by the oxidizing-agent alone. An example will make this plain. Bromic acid, $HBrO_3$, has practically no oxidizing action on arsenious acid; sulphurous acid, however, is oxidized by bromic acid almost instantaneously. Now, in case sulphite is added to a mixture of bromic acid and arsenious acid, not only the sulphurous acid but also a part of the arsenious acid is oxidized.

Such actions are frequently observed; they are called **coupled, or induced, reactions.** Their general scheme is as follows:

A + B→Reaction;

A + C→Practically no reaction;

A + B + C→Reaction between A and C, as well as between A and B.

A second example of a coupled reaction is the following: Arsenious oxide is oxidized by chromic acid but not by bromic acid. However, when all three substances are mixed, the bromic acid is also partially reduced. We may formulate the case as follows:

$H_2CrO_4 + As_2O_3 \rightarrow$ Reaction;

$HBrO_3 + As_2O_3 \rightarrow$ No reaction;

$H_2CrO_4 + HBrO_3 + As_2O_3 \rightarrow$ Reduction of both chromic and bromic acids.

While in the first example the reaction between bromic acid and arsenious acid is induced by a reducing-agent (sulphurous acid), in the second case this is accomplished by an oxidizing-agent (chromic acid).

For the purpose of classification general names have been given to the three substances which participate in a coupled reaction. The substance *A* of the above scheme is termed the *actor*, the substance *B*, which reacts with *A* alone, is called the *inducer*, while *C*, the substance that is only attacked in company with *A* and *B*, is known as the *acceptor*. The first example may be annotated thus:

$$\underset{\text{Actor.}}{HBrO_3} + \underset{\text{Inducer.}}{H_2SO_3} \rightarrow \text{Reaction.}$$

$$\underset{\text{Actor.}}{HBrO_3} + \underset{\text{Acceptor.}}{As_2O_3} \rightarrow \text{No reaction.}$$

$$\underset{\text{Actor.}}{HBrO_3} + \underset{\text{Inducer.}}{H_2SO_3} + \underset{\text{Acceptor.}}{As_2O_3} \rightarrow \left\{ \begin{array}{l} \text{Reaction both between } HBrO_3 \text{ and } H_2SO_3 \\ \text{and between } HBrO_3 \text{ and } As_2O_3. \end{array} \right.$$

The inducer and acceptor are similar to each other, but opposite to the actor, in chemical behavior, as may be readily seen in the second example.

The ratio of the transformed portions of the acceptor and inducer is termed the induction factor, thus:

$$\frac{\text{Equivalents of the acceptor transformed}}{\text{'' '' '' inducer ''}} = \text{Induction factor.}$$

This factor is not constant for a definite coupled reaction but varies, for instance, with the concentration of the substance concerned, as well as with other circumstances. The cause of this dependence on the concentration is readily perceived. The velocity of a reaction is proportional to the concentration of the interacting substances. If the concentration of the acceptor is increased, more of the acceptor will react with the actor than before; the induction factor will, therefore, become larger. If, on the contrary, the concentration of the inducer is increased, the factor must diminish.

Among coupled, or induced, reactions must also be classed the various instances of *oxygen activation*. The meaning of this term is best understood from an example. Sodium sulphite is readily oxidized by free oxygen to the sulphate. Sodium arsenite, however, is not oxidized by it when the solution contains an excess of acid potassium carbonate. But, if the mixed solution of these salts is shaken up with air (actor), both the sulphite (inducer) and the arsenite (acceptor) are oxidized, and both consume exactly the same amount of oxygen. This is also true for other such oxygen activations.

To explain the phenomena presented by coupled reactions it is assumed that the actor or the inducer in their complete reduction or oxidation pass through intermediate stages, the intermedial substances being also able to oxidize the acceptor. In the above examples the intermedial product might be bromous acid, $HBrO_2$. As a matter of fact such intermedial substances have been isolated in some cases, or their existence has been at least rendered very probable. The consumption of just as much oxygen by the inducer as by the acceptor in oxygen activations is explained by supposing that the inducer is oxidized by an oxygen molecule to a "peroxide," which then yields an atom of oxygen to the acceptor. An example, for which this has been actually proved, is found in the oxidation of benzaldehyde in the presence of indigosulphonic acid. *Cf.* ORG. CHEM., § 299.

ARSENIC ACID, H_3AsO_4.

162. This acid is most easily obtained by the oxidation of a solution of arsenious acid by warming it with nitric acid. On concentrating the solution the compound $2H_3AsO_4+H_2O$ separates out (below 15°); this substance gives off its water of crystallization at 100° and yields *orthoarsenic acid*, H_3AsO_4, which crystallizes in fine needles. When heated further it gives off water (at 180°) and goes over into *pyroarsenic acid*, $H_4As_2O_7$, which separates in the form of hard glistening crystals. On being heated still higher the latter compound gives up another molecule of water, the final product being white crystalline *meta-arsenic acid*, $HAsO_3$. This conduct is completely analogous to that of phosphoric acid; however, metaphosphoric acid cannot be converted into the anhydride by heat as can arsenic acid (§ 160). The pyro- and meta-arsenic acids are stable only in the solid state; when treated with water they are converted into the ortho acid, the transformation being much quicker than with the corresponding phosphorous acids.

Orthoarsenic acid is easily soluble in water. Its salts, the arsenates, exist in three classes; of the tertiary only those of the alkalies are soluble in water. The reactions of arsenic acid are very similar to those of phosphoric acid (§ 146); in this case also a mixture of ammonia, ammonium chloride and magnesium sulphate (*magnesia mixture*) precipitates a white crystalline ammonium magnesium salt, $Mg(NH_4)AsO_4+6H_2O$. Ammonium molybdate produces a yellow finely crystalline precipitate, whose composition and appearance correspond to those of the phosphorus compound. The precipitates formed with silver nitrate are, however, unlike in color: Ag_3PO_4 is yellow, Ag_3AsO_4 reddish brown.

Sulphur Compounds of Arsenic.

163. Three are known: *arsenic disulphide* (*realgar*), As_2S_2; *arsenic trisulphide* (*orpiment*), As_2S_3; *arsenic pentasulphide*, As_2S_5.

Arsenic disulphide, As_2S_2,

occurs in nature as *realgar* (§ 155). It forms beautiful ruby-red crystals of a specific gravity of 3.5. It is used as a pigment. It is manufactured artificially by fusing sulphur and arsenic together; the resulting products vary in composition, however.

ARSENIC TRISULPHIDE, As_2S_3.

Arsenic is precipitated from the acid solution of arsenious oxide by sulphuretted hydrogen as sulphide; in this respect too it behaves as a heavy metal. In the above reaction arsenic trisulphide is deposited as an amorphous yellow powder. A pure solution of arsenious acid gives no precipitate with sulphuretted hydrogen, but simply a yellow liquid (§ 195). Arsenic trisulphide occurs in nature as *orpiment* (§ 155), having a laminated crystalline structure; it owes its name to its beautiful golden lustre. By fusing artificial arsenic trisulphide a product is obtained which is very similar to the natural orpiment, but has a lower specific gravity (2.7 instead of 3.4). Commercially the trisulphide is prepared by fusing white arsenic with sulphur; the product still contains the oxide, however, and is therefore poisonous. Arsenic trisulphide is insoluble in water and in acids.

ARSENIC PENTASULPHIDE, As_2S_5.

After sulphuretted hydrogen has been led into a warm acidulated solution of arsenic acid for some time, arsenic is precipitated as an amorphous yellow powder of the composition As_2S_5. The latter is also obtained by fusing arsenic trisulphide with the required amount of sulphur. In the absence of air it can be sublimed without decomposition. It is insoluble in water and in acids.

SULPHO-SALTS OF ARSENIC.

164. The trisulphide and the pentasulphide of arsenic dissolve easily in alkali sulphides, forming salts of *sulpho-acids:*

$$As_2S_3+3K_2S=2\underset{\substack{\text{Pot. sulph-}\\ \text{arsenite.}}}{K_3AsS_3};$$

$$As_2S_5+3K_2S=2\underset{\substack{\text{Pot. sulph-}\\ \text{arsenate.}}}{K_3AsS_4}.$$

The formation of these sulpho-salts can be regarded as analogous to that of an oxy-salt from a basic oxide and an acid anhydride, e.g.:

$$BaO+SO_3=BaSO_4.$$

The trisulphide and the pentasulphide are therefore to be considered as *sulpho-anhydrides* of those sulpho-acids.

The sulpharsenates can also be obtained from arsenic trisulphide with the aid of an alkali polysulphide:

$$As_2S_3 + K_2S_3 = \underset{\text{Pot. sulpho-meta-arsenate.}}{2KAsS_3}.$$

This reaction can be explained by supposing that the arsenic trisulphide is converted into the pentasulphide by the excess of sulphur, just as the trioxide is oxidized to the pentoxide.

They are also produced by treating an arsenate with hydrogen sulphide:

$$K_3AsO_4 + 4H_2S = K_3AsS_4 + 4H_2O.$$

The sulpharsenates and sulpharsenites of the alkalies dissolve easily in water and can be obtained in the crystalline form from the solution; those of the other metals are insoluble The free sulpho-acids are unknown. On the addition of an acid to the solution of a sulpho-salt, the liberated sulpho-acid breaks up into hydrogen sulphide and arsenic tri- or pentasulphide.

ANTIMONY.

165. Antimony occurs in nature in *stibnite*, Sb_2S_3, as well as in many less common minerals. Stibnite was known to the ancients. In Japan it is found in magnificent large crystals. Antimony was frequently employed by the alchemists. Basilius Valentinus in the latter part of the fifteenth century described its extraction from stibnite in a monograph entitled "The triumphal car of Antimonium."

The element is at present obtained from stibnite by two processes. In one the mineral is roasted, being thus transformed into antimonious oxide. This oxide is then reduced with charcoal to metallic antimony:

$$\text{I. } 2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2;$$
$$\text{II } 2Sb_2O_3 + 3C = 4Sb + 3CO_2.$$

The other method is to fuse the mineral with iron:

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

The crude antimony thus obtained usually still contains arsenic, lead, sulphur, etc. It can be refined by fusing with a little saltpetre, the impurities being oxidized.

Physical Properties.—Antimony is silvery-white and has a high metallic lustre and a laminate-crystalline structure (rhombohedral); as a result of the latter it is very brittle and can be easily pulverized. Sp. g. =6.71–6.86. Melting-point, about 632°; boiling-point, 1450°. MENSCHING and V. MEYER succeeded in determining the vapor density at 1437°, i.e. slightly below the boiling-point, and found that the molecule, unlike that of phosphorus or arsenic, consists of less than four atoms.

Like arsenic antimony has a black and a yellow modification; the latter is obtained by passing air into liquid stibine, cooled to −90°. It is even less stable than the yellow arsenic.

Chemical Properties.—At ordinary temperatures the element is not affected by the air; when heated, it burns with a bluish-white flame to the trioxide. It combines with the halogens directly, producing scintillations (§ 27). It is dissolved by hydrochloric acid, although very slowly, with the evolution of hydrogen, thus asserting its metallic character. Aqua regia dissolves it readily.

Uses.—Antimony is a constituent of various alloys. The most important of these is type-metal, from which printer's type is made. Its approximate compostion is lead (50%), antimony (25%) and tin (25%).

HYDROGEN ANTIMONIDE, STIBINE, SbH_3.

166. Stibine is formed when nascent hydrogen acts on a soluble antimony compound. It is best prepared by treating an alloy of one part of antimony and two parts of magnesium with dilute hydrochloric acid. The product consists principally of hydrogen, but contains 10–14% SbH_3. If this gas mixture is passed through a U-tube and the whole is plunged in liquid air, stibine condenses to a white solid mass, that soon melts after the tube is removed from the liquid air. It vaporizes to a relatively stable gas. The least trace of oxygen, however, causes some antimony to be deposited.

If an electric spark is passed through stibine gas it explodes, antimony is set free and the volume of hydrogen liberated is found to be 1½ times that of the stibine, which is in accord with the formula SbH_3. It is also decomposed rapidly by heating the containing vessel above 150°.

Stibine has a characteristic musty odor, quite unlike that of phosphine or arsine.

When the mixture of hydrogen and stibine evolved from the alloy of antimony is heated, as in the MARSH experiment (§ 157), it produces a metallic mirror and, when ignited, the flame gives a spot on cold porcelain similar to that of arsenic, but differing from the latter in its darker color, insolubility in hypochlorite solution and less volatility when heated in a current of hydrogen. Stibine precipitates a black powder from silver solution, consisting of a mixture of silver and silver antimonide, Ag_3Sb.

Halogen Compounds of Antimony.

167. Two compounds of this element with chlorine are known: $SbCl_3$ and $SbCl_5$.

Antimony trichloride, $SbCl_3$, is obtained by treating antimony sulphide or oxide with concentrated hydrochloric acid. It forms a colorless laminar-crystalline mass, which is so soft that it was formerly known as "antimony butter" (*butyrum antimonii*). Its melting-point is 73.5° and its boiling-point 223.5°; its vapor density 7.8 (air = 1) makes the formula $SbCl_3$.

It dissolves in water containing hydrochloric acid. Water decomposes it, forming difficultly soluble oxychlorides. The composition of the precipitate depends on the amount and the temperature of the water used in the decomposition. There is evidence of the existence of the compounds $SbOCl$ and $Sb_4O_5Cl_2$ ($=2SbOCl, Sb_2O_3$), both of which crystallize. The precipitated oxychlorides on being repeatedly boiled with water eventually lose all their chlorine and go over into the trioxide, Sb_2O_3.

Powder of Algaroth, once used in medicine, is obtained by the decomposition of antimony trichloride with water and has nearly the same formula as the second of the above-mentioned oxychlorides.

Antimony pentachloride, $SbCl_5$, is prepared by heating antimony in a current of chlorine or treating fused trichloride with chlorine. It is a yellow, fuming, ill-smelling liquid, which crystallizes at −6°. When heated it dissociates into the trichloride and chlorine. It unites with water, forming $SbCl_5 \cdot H_2O$ and $SbCl_5 \cdot 4H_2O$. Hot water decomposes it into hydrochloric and pyroantimonic acids.

Oxygen Compounds of Antimony.

168. Three are known: *antimony trioxide*, Sb_2O_3, *antimony tetroxide*, Sb_2O_4, and *antimony pentoxide*, Sb_2O_5.

Antimony trioxide occurs as a mineral, *senarmontite*. It can be obtained by burning antimony in the air, as well as by the oxidation of antimony with dilute nitric acid. It is dimorphic, occurring in both regular and rhombic crystals.

It is a light yellow crystalline powder, almost insoluble in water. It volatilizes at 1560° the vapor density at this temperature corresponds to the formula Sb_4O_6. It is insoluble in sulphuric and nitric acids but easily soluble in hydrochloric and tartaric acids and in alkalies. On being heated in the air it turns to the tetroxide.

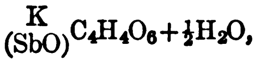
The corresponding hydroxide is $Sb(OH)_3$. This hydrate separates out when tartar emetic (see below) is decomposed with dilute sulphuric acid. It gives up one molecule of water readily and passes over into the hydroxide $SbO \cdot OH$, *meta-antimonious acid*.

The latter is more easily obtained by treating a solution of the trichloride with soda solution:

$$2SbCl_3 + 3Na_2CO_3 + H_2O = 2SbO \cdot OH + 6NaCl + 3CO_2.$$

It appears as a white precipitate, which is converted into antimonic oxide by boiling with water. This meta-antimonious acid is dissolved by alkalies, forming salts of the acid. One of them which has been obtained crystallized is the sodium meta-antimonite, $NaSbO_2 + 3H_2O$. The latter is difficultly soluble in water, and decomposes on concentration of its solution.

On the other hand, antimony hydroxide displays basic properties by uniting with acids to form salts. There are salts known of $Sb(OH)_3$, as well as of $SbO \cdot OH$. Examples of the former kind are the crystallized *antimony sulphate*, $Sb_2(SO_4)_3$, and the *nitrate*, $Sb(NO_3)_3$. In analogy with other trivalent metals double salts are known, e.g. $KSb(SO_4)_2$. As to the salts derived from $SbO \cdot OH$, we may look upon the group SbO as taking the place of a univalent metal. Thus $SbO \cdot OH$ may be compared with KOH. For this reason the group (SbO) has been given the name *antimonyl;* one of its salts is *antimonyl sulphate*, $(SbO)_2SO_4$. The most familiar antimonyl compound is *tartar emetic*, potassium antimonyl tartrate,



$$\substack{K\\(SbO)}C_4H_4O_6+\tfrac{1}{2}H_2O,$$

which is employed in medicine. It is prepared by boiling acid potassium tartrate (*cream of tartar*) with antimony oxide and water; tartar emetic is readily soluble in water.

ANTIMONY PENTOXIDE AND ANTIMONIC ACID.

Antimonic acid, H_3SbO_4, is obtained by warming antimony with concentrated nitric acid and also by decomposing the pentachloride with water. It is a white powder, almost insoluble in water and nitric acid; nevertheless, when moist, it turns litmus paper red. On heating saltpetre with powdered antimony the potassium salt of *meta-antimonic acid*, $KSbO_3$, is formed in an explosive reaction. When this is boiled with water it dissolves, producing *monopotassium orthoantimoniate*, KH_2SbO_4; on fusing with potash *potassium pyroantimoniate*, $K_4Sb_2O_7$, is formed, which dissolves in water, giving 2KOH and $K_2H_2Sb_2O_7+6H_2O$. In the case of antimony, as in that of phosphorus, we meet with three kinds of acids belonging to the highest stage of oxidation: their formulæ correspond to those of the analogous phosphorus compounds.

Antimony pentoxide, Sb_2O_5 (molecular weight unknown), can be obtained by heating antimonic acid at 300°. It is a yellow amorphous powder, soluble in hydrochloric acid. If heated strongly it gives up part of its oxygen and goes over into **antimony tetroxide,** Sb_2O_4, a white powder that turns yellow on heating but resumes its original color on cooling. This tetroxide can be regarded as *antimonyl meta-antimoniate*, $SbO_3 \cdot SbO$.

Sulphur Compounds of Antimony.

169. **Antimony trisulphide,** Sb_2S_3, is found in nature (§ 165). It can be made by leading hydrogen sulphide into a hydrochloric acid solution of the trichloride, from which it is deposited as an amorphous red powder. It can be melted; on cooling it crystallizes and takes on the appearance of stibnite.

Antimony pentasulphide, Sb_2S_5, is precipitated when hydrogen sulphide is passed into the acidified solution of antimonic acid. It is more easily obtained by the decomposition of sodium sulphantimoniate with dilute sulphuric acid. It forms an amorphous orange-red powder, which splits up into sulphur and the trisulphide on being strongly heated. It is insoluble in dilute acids; boiling-hot concentrated hydrochloric acid dissolves it, forming antimony trichloride, hydrogen sulphide and sulphur. In aqueous solutions of alkalies and their sulphides it dissolves easily with the formation of sulphantimoniates, M_3SbS_4 The best known of these is *sodium sulphantimoniate*, $Na_3SbS_4+9H_2O$ ("SCHLIPPE's salt"). It can be obtained by boiling antimony trisulphide with sulphur and caustic soda solution. It crystallizes in large colorless tetrahedrons, is easily soluble in water (1 part by weight in 2.9 parts water at 15°) and reacts alkaline. It is decomposed by acids, depositing pentasulphide; even carbonic acid causes this, hence the crystals become covered with a yellowish-red coating of pentasulphide after having stood some time in the air. The free sulphantimonic acid is not known.

BISMUTH.

170. This element belongs undoubtedly among the metals, so far as its physical character is concerned; its chemical properties also class it with them in almost every respect, inasmuch as its oxides are mainly basic in their behavior.

It is found chiefly in the native state; but a sulphide, Bi_2S_3, *bismuth glance* and a telluride, *tetradymite*, also occur in nature. Bismuth is obtained from the latter by roasting to the oxide Bi_2O_3 and reducing with charcoal. The native metal is usually very pure. If refining is necessary, the fused metal is allowed to flow over a hot, somewhat inclined iron plate, so that the impurities are oxidized. The amount of bismuth found in nature is not very great.

Physical Properties.—Bismuth is externally very similar to antimony; it is crystallized and very brittle and has a metallic lustre, but differs from antimony in having a reddish-white color. Sp. g.=9.823. It melts at 286.3° and boils above 1090°. It can be distilled in a current of hydrogen.

Chemical Properties.—At ordinary temperatures bismuth is unaffected by the air. On being heated it turns to the trioxide. It combines with the halogens directly. It is not attacked by hydrochloric or sulphuric acid at ordinary temperatures, but nitric acid dissolves it readily to form the nitrate. On being heated with sulphuric acid, it gives off sulphur dioxide and forms the sulphate. No hydrogen compound of bismuth is known.

Bismuth is employed in the manufacture of easily fusible alloys such as are used in making casts of woodcuts, stereotypes, etc. The most common of these alloys are NEWTON's metal (8 bismuth, 5 lead, 3 tin; melting-point 94.5°), ROSE's metal (2 bismuth, 1 lead, 1 tin; melting-point 93 75°) and WOOD's metal (4 bismuth, 2 lead, 1 tin, 1 cadmium; melting-point 60.5°).

Halogen Compounds.

171. Compounds of the type BiX_3 only are known. **Bismuth chloride,** $BiCl_3$, is formed by direct synthesis from the elements, but more easily by dissolving bismuth in aqua regia. It is white and crystallized. Its melting-point is between 225° and 230° and its boiling-point at 435°. Its vapor density, 11.35 (air = 1), gives it the formula $BiCl_3$. On being dissolved in a little water it forms a sirupy liquid; an excess of water gives **bismuth oxychloride,** $BiOCl$, and hydrochloric acid. This oxychloride is a white powder, insoluble in water but soluble in acids.

Oxygen Compounds.

172. Three oxides are known: BiO, Bi_2O_3, and BiO_2.

Bismuthous oxide, BiO, is obtained by adding an alkaline stannous chloride solution to a solution of bismuth chloride. It is deposited as a dark-brown precipitate of BiO. When heated in the air it smolders like tinder. It is doubtful whether this precipitate is a homogeneous substance or a mixture of Bi_2O_3 with finely divided bismuth.

Bismuth trioxide, Bi_2O_3, is the most familiar oxide of this element. It has strictly basic properties. In order to prepare it we can heat the nitrate or carbonate or we can precipitate the hydroxide from the solution of a bismuth salt by means of a base and heat the precipitate. If a boiling solution of a bismuth salt is treated with caustic potash, the trioxide separates out in glistening needles of microscopic dimensions. Like the corresponding oxides of arsenic and antimony, it is dimorphic

Bismuth dioxide, BiO_2, has been little studied; it is a reddish-yellow powder.

Hydroxides and Salts.

173. **Bismuth hydroxide,** $Bi(OH)_3$, is obtained by precipitating a bismuth salt with an alkali. It is an amorphous white powder, insoluble in potassium hydroxide or ammonia. At 100° it goes over into the compound $BiO\cdot OH$ with the loss of a molecule of water. Both of these hydroxides are wholly basic in character. The salts derived from $Bi(OH)_3$ are called neutral, those from $BiO\cdot OH$ basic.

The *neutral nitrate*, $Bi(NO_3)_3$, is obtained by dissolving bismuth in nitric acid. It crystallizes with five molecules of water in large translucent triclinic prisms. It is deliquescent. The addition of much water converts it into the *basic nitrates*, several of which are known. By treating the neutral nitrate with about 20 parts of boiling water a product is obtained whose composition is not perfectly constant for different preparations, but corresponds nearly to the formula $(Bi_2O_3)_6\cdot(N_2O_5)_5\cdot(H_2O)_9$, or $2BiONO_3 + Bi(NO_3)_3 + 3Bi(OH)_3$. This is the **bismuth subnitrate,** which is used in medicine.

Bismuth sulphate, $Bi_2(SO_4)_3$, is obtained as an amorphous white substance when the metal is heated with concentrated sulphuric acid. With water it forms a basic sulphate, $Bi_2(OH)_4SO_4$.

Sulphur Compounds.

174. **Bismuth trisulphide** is found in nature (§ 170); artificially it can be prepared by heating bismuth with sulphur or by leading hydrogen sulphide into the aqueous solution of a bismuth salt. In the latter case it comes down as an amorphous black powder that is easily soluble in warm dilute nitric acid. It is insoluble in alkalies and their sulphides, hence forms no sulpho-salts. When heated with an alkali sulphide solution to 200° it takes on a crystalline form similar to that of the natural mineral.

SUMMARY OF THE NITROGEN GROUP.

175. Like the halogens and the elements of the oxygen group, the elements just discussed, viz. nitrogen, phosphorus, arsenic, antimony and bismuth, also form a natural group. Their family relation shows itself even in the formula types of their compounds. The hydrogen compounds have the type RH_3 (lacking with bismuth), the halogen compounds RX_3 and RX_5 (the latter also lacking with bismuth), the oxygen compounds R_2O_3 and R_2O_5. In other words, the elements of this group are trivalent or pentivalent. We find here, just as in the groups previously studied, that, as the atomic weight increases, a gradual change occurs in the physical properties. This is shown by the following small table:

	N.	P.	As.	Sb.	Bi.
Atomic weight. . .	14.04	31.0	75.0	120.2	208.5
Specific gravity. . . (Water = 1)	0.885 liquid	1.8 − 2.1	4.7 − 5.7	6.7	9.8
Melting-point. . . .	....	+44.4°	ca. 500°	+430°	+268°
Boiling-point.	−194.4°	+278°	....	at white heat	
Color.	colorless	yellow or red	gray	white	pink

In the chemical properties, also, regular variations are to be observed, all of which can be summed up in the general statement that the metalloid character gives way to the metallic character as the atomic weight increases. Nitrogen forms either indifferent or acid-forming oxides only; so does phosphorus; arsenic, on the contrary, displays a very feebly basic character in arsenious oxide, since this oxide forms the trichloride with hydrochloric acid, the trichloride reacting inversely with water, however, and breaking up into hydrochloric acid and arsenious oxide. In antimony trioxide this basic character is a little stronger; some salts and double salts of it with acids are known. The corresponding chloride does not suffer an immediate hydrolytic dissociation with water, but oxychlorides are formed, which require a great deal of water to convert them entirely into the trioxide. While the highest oxides of arsenic and antimony have strictly acid properties, with bismuth the acidic nature has practically disappeared; the oxide Bi_2O_3 has exclusively basic properties and the higher oxide Bi_2O_5 acts like a peroxide, giving off oxygen readily (it generates chlorine with hydrochloric acid) and going over into the lower oxide Bi_2O_3. Bismuth trichloride, $BiCl_3$, gives the oxychloride, BiOCl, with water and this is not decomposed by an excess of water.

In the hydrogen compounds, too, the gradual change of the properties is very apparent. Consider the stability for example: ammonia requires a very high temperature for decomposition; phosphine and arsine a much lower temperature; stibine is unstable at ordinary temperatures when it comes in contact with oxygen, and the hydrogen compound of bismuth is so unstable that the conditions for its formation and existence have not yet been ascertainable. A similar change is noticeable in their ability to form $XH_4^{\cdot}$ ions in aqueous solutions; it is strong in ammonia, much weaker in phosphine and wholly absent in arsine and stibine.

In the sulphur compounds a progressive change of color is observed. P_2S_5 is bright yellow, As_2S_5 deep yellow, Sb_2S_5 red and Bi_2S_5 black. The first three are sulpho-anhydrides of sulpho-acids (§ 164); bismuth sulphide is not, however, thus displaying again the more basic nature of bismuth.

CARBON.

176. Carbon occurs in nature both free and combined. In combination it is found in large quantities in the salts of carbonic acid, above all in calcium carbonate, *limestone*, which is of the widest occurrence and is even known to form great mountains. Farther, carbon is one of the constituent elements of animals and plants. It is found in these in numerous compounds. Still larger is the number of artificially prepared carbon compounds. The compounds of carbon exceed in number all other compounds together. For this reason and because of the peculiarities of the carbon compounds it is customary to treat them by themselves, as " organic chemistry." However, that we may be able to obtain a general survey of the elements, it is deemed advisable to discuss certain compounds of carbon in inorganic chemistry as well.

Allotropic Forms of Carbon.

We know of three: *diamond, graphite* and *amorphous carbon.*

(*a*) **Diamond.**—LAVOISIER proved that this mineral consists of carbon.

As early as the seventeenth century ANSELMUS DE BOOT and NEWTON suspected that the diamond must be capable of burning because of its strong refractive power; not, however, until the year 1694 were experiments on this point undertaken. At the instigation of COSMOS III., Grand Duke of Tuscany, AVERANI and TARGIONI, members of the Academia del Cimento at Florence, then discovered that a diamond would burn in the focus of a concave mirror. Subsequently FRANÇOIS ETIENNE DE LORRAINE found that it also burns in a blacksmith's forge. As the diamond was then almost universally regarded as a very pure sort of quartz, these observations were little heeded. In the years 1766–1772, however, experiments were again instituted with wonderful care and precision by numerous French scholars in co-operation (among them D'ARCET, ROUELLE, CADET, MACQUER and LAVOISIER), to whom the leading Parisian jewelers at first furnished diamonds without cost. Their investigations revealed that diamond when heated away from air remains unchanged, but burns on the admission of air. Later LAVOISIER showed that carbon dioxide is formed from this combustion, and in 1814 DAVY proved that, when diamond burns, nothing else than this gas is formed, so that diamond must be pure carbon. Further, it was found by KRAUSE in 1890 that, when the carbon dioxide given off by the combustion of diamond is absorbed by sodium hydroxide, a soda is produced which is in every respect identical with ordinary soda. Finally it has been possible to manufacture diamonds from amorphous carbon (see below).

The diamond crystallizes in the isometric system. Usually it is colorless, but yellow and black diamonds are also known; the black ones are called *carbonado.* The specific gravity of diamond is 3.50–3.55. It is a poor conductor of heat and electricity. The refractive index is very high: $n=2.42$. The diamond is so hard that it scratches all other substances. If it is subjected to a very high temperature in the absence of air, it gradually turns to graphite. It resists the action of the strongest oxidizing-agents, e.g. a mixture of nitric acid and potassium chlorate.

In 1893 MOISSAN succeeded in making diamonds artificially, although they were very small, the largest being about 0.5 mm. in diameter. His method consists essentially in dissolving carbon in molten iron at a high temperature and then cooling it rapidly.

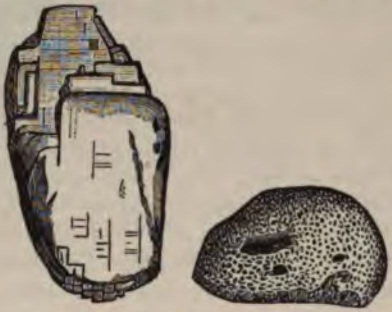


FIG. 42.—ARTIFICIAL DIAMONDS (MAGNIFIED).

This is accomplished as follows: Iron is brought in contact with pure carbon (sugar charcoal) in the electric furnace at a high temperature. After the iron has become saturated with carbon at about 3000°, the fused mass is suddenly cooled by pouring it into a hole drilled in a copper block, which is kept cold by water, and at once covering the cavity with an iron stopper. When the iron is all cold it is dissolved away by acids, leaving the carbon which did not combine with the iron. This residual carbon consists partly of small diamonds, which are identical with the natural diamond in hardness, crystal form, etc. Fig. 42 presents an enlarged view of some artificial specimens; they display the same properties as the rough natural diamonds, particularly the rounded edges and angles and the striations.

The formation of the diamond by this method has been explained by BAKHUIS ROOZEBOOM as follows: In all probability the transition of diamond into graphite is endothermic. For this reason diamond is the more stable form at lower temperatures, graphite at higher ones, in analogy to the rhombic and monoclinic modifications of sulphur. But, while the velocity of transformation of monoclinic sulphur is fairly great at low temperatures and the monoclinic sulphur can thus exist only for a short time below its transition point, the transition velocity of graphite into diamond is practically zero for temperatures below 1000°. Carbon that has crystallized from molten iron in the form of graphite cannot, therefore, pass over into diamond. The rapid cooling of the molten iron, however, has the effect of bringing the carbon into the region of temperature in which diamond is the stable modification; it can therefore separate in this form from its solution.

The electric furnace that MOISSAN used for these and numerous other experiments is very simple in construction. It consists of two blocks of unslaked lime that fit tightly together. In the lower block there is a trough in which the carbon terminals are laid. The upper block is slightly hollowed out on its lower side so as to reflect the heat rays on to the crucible. Fig. 43 shows a cross-section of an electric furnace, Fig. 44 a picture of the same apparatus in operation.

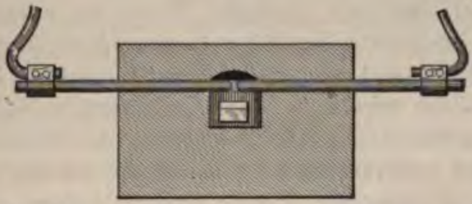


FIG. 43.—MOISSAN'S ELECTRIC FURNACE (CROSS-SECTION).

The temperatures obtained in the electric furnace are as follows:

Current of 30 ampères and 55 volts with a steam-engine of 4 H.P., 2250°
" " 100 " " 45 " " " " " 8 " 2500°
" " 450 " " 70 " " " " " 50 " 3000°

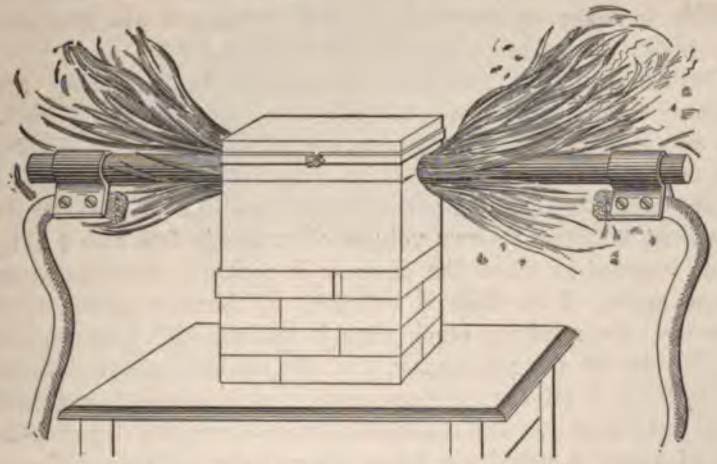


FIG. 44.—MOISSAN'S FURNACE IN OPERATION. (AFTER MOISSAN.)

The last-named temperature can however only be maintained for a brief period, as the unslaked lime soon melts and flows like water. At 2500° the lime becomes crystalline in structure after a few minutes.

(*b*) **Graphite** is also crystallized carbon. Unlike diamond, it is very soft and opaque and a good conductor of heat and electricity. Sp. g.=2.09–2.23. As was stated above, graphite can be prepared artificially by the crystallization of carbon from molten iron and by heating diamond strongly. There are various kinds of graphite. If graphite is treated with a mixture of perfectly dry potassium chlorate and very concentrated nitric acid, it turns to a yellow crystallized substance containing hydrogen and oxygen, in addition to carbon, and called *graphitic acid*. This substance is peculiar in that it decomposes explosively on heating and yields a large volume of extremely fine amorphous carbon. Graphite is used in the manufacture of lead pencils, crucibles, electrodes, polishes, etc.

(*c*) **Amorphous Carbon.**—This is obtained in the purest state by charring sugar. The resulting mass is boiled with acids to remove the mineral matter and finally heated red-hot in a current of chlorine for quite a while to remove all the hydrogen. It can also be prepared from soot. Amorphous carbon is opaque, black and infusible. At the highest temperature that MOISSAN could reach with his furnace by employing a current of 2000 ampères and 80 volts (obtained with a 300 horse-power engine) it was barely possible to make carbon sublime. The sublimate was graphite. Amorphous carbon has a specific gravity of 1.5–2.3.

Various sorts of amorphous carbon are known. They are probably different allotropic modifications, or mixtures of such. *Gas carbon* and *coke* are obtained as residues in the dry distillation of coal. They conduct heat and electricity. *Wood charcoal* is very porous and can condense large quantities of gases in its pores, e.g. 90 times its own volume of ammonia (see also § 111). When warmed or when the pressure is reduced, these gases all escape again. *Bone-black* is obtained by heating bones away from air; the resulting black mass is treated with hydrochloric acid to remove the phosphates and carbonates present. It has the power of absorbing coloring-matter and certain salts, e.g. lead salts, from liquids. The charcoal obtained from the dry distillation of sugar is noted for its peculiar lustre. These different sorts of charcoal do not consist of pure carbon but contain other substances in small proportions. It is a general rule that carbon conducts heat and electricity better the longer it has been exposed to a high temperature.

177. The various kinds of carbon all find their respective uses. *Soot, or lampblack,* serves for the preparation of India ink and black paint. *Gas carbon* (*coke*), being a good conductor of electricity, is used in the electrical industry. *Wood charcoal* is used in the manufacture of gunpowder; *animal charcoal,* or *bone-black,* as a water-filter to remove coloring-matter, ill-smelling gases or injurious salts (lead salts) from drinking-water; it is also employed in enormous quantities in sugar refineries to decolorize sugar liquids.

By far the most important use of carbon is as a fuel. The heat generated by the burning of coal warms our houses, drives our steam-engines, etc.

The principal kinds used as fuels are *charcoal, coke, anthracite coal, bituminous coal, brown coal* (*lignite*) and *peat.*

Charcoal (wood charcoal) is made on a large scale by the colliers. Long sticks of wood are piled in a large heap, covered with sod and ignited at the bottom. The wood smolders away slowly and becomes completely charred. This "charcoal-pit" process is not at all economical, inasmuch as all the volatile products are lost; it is carried on extensively (Fig. 45), but it is being more and more replaced by the dry distillation of wood from iron retorts, in which process the gaseous and tarry products are recovered.

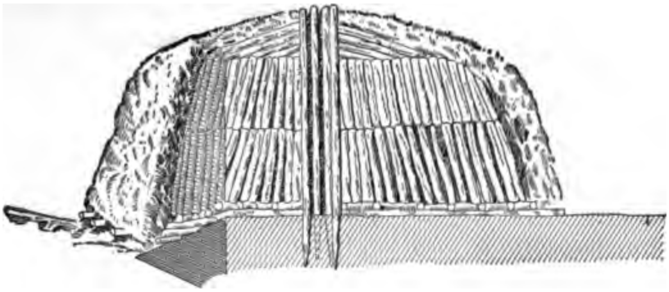


FIG. 45.—CHARCOAL PIT.

Coke is the residue in the retorts of the gas factories after the coal has been deprived of its volatile products by heating. It is also manufactured on a large scale for metallurgical and other purposes. Coke is thought by many to have a great future as a fuel, since it is a hard-burning smokeless fuel, manufactured from the cheap soft coal.

Peat and the *various coals* owe their origin to the same geological process, the slow decay of plant-remains in the absence of air. Peat is the youngest formation and anthracite coal the oldest. During this transition carbon dioxide and methane, CH_4, are given off and the residue becomes richer in carbon and poorer in hydrogen and oxygen than the corresponding chief constituent of plant tissues, cellulose. The following table shows this:

	Carbon.	Hydrogen.	Oxygen.
Cellulose	50.0%	6.0%	44.0%
Peat	60.0	5.9	34.1
Brown coal	67.0	5.8	27.2
Cannel coal	85.8	5.8	8.3
Anthracite coal	94.0	3.4	2.6

The plants of which these formations originally consisted are different. Peat appears from its structure to have come chiefly from swampy growths, mosses and the like; mineral coal from extinct plants, gigantic horsetails (equiseta), lepidodendra and sigillariæ.

Molecular and Atomic Weight of Carbon.—Chemical Properties.

178. The carbon molecule probably contains a large number of atoms. It has not yet been possible to determine how large this number is. It is supposed that graphite has a larger number of atoms to the molecule than amorphous carbon, and diamond more than graphite, since graphite and diamond are less easily attacked by chemical reagents and because they are denser.

A determination of the vapor density of carbon is of course out of the question. The measurement of the melting-point depression that carbon produces in iron is also impracticable; however, it is known that even a small percentage of carbon causes a considerable lowering of the melting-point of iron (see § 304).

It can be shown in the following way, however, that the number of atoms in the carbon molecule must be very great. By the oxidation of amorphous carbon with potassium permanganate *mellitic acid* is formed, which contains 12 carbon atoms to the molecule. This makes it quite probable that the carbon molecule contains at least 12 atoms, for in the oxidation of organic substances the products almost always contain either a smaller or the same number of carbon atoms to the molecule. For the following reason it is, however, to be supposed that the number of atoms in the carbon molecule is much greater than 12. When *marsh-gas*, CH_4, is passed through a red-hot tube, *ethylene*, C_2H_4, is formed among other things. If this is then treated in the same way, *acetylene*, C_2H_2, is obtained, and from this again *benzene*, C_6H_6. On conducting benzene vapor through a glowing tube, *naphthalene*, $C_{10}H_8$, *pyrene*, $C_{16}H_{10}$, etc., are formed. If either of the latter is heated still higher (in the absence of air) carbon is deposited. We thus see that as the temperature rises the number of carbon atoms in the molecule steadily increases. The final product of these operations, carbon, will therefore probably contain a considerably larger number of atoms in its molecule than naphthalene or pyrene.

Carbon can unite directly with many elements. At ordinary temperatures it combines with fluorine only. MOISSAN introduced lampblack into fluorine gas, and the carbon commenced to glow; when fluorine was present in excess *carbon tetrafluoride*, CF_4, was formed.

Hydrogen combines with carbon directly to form acetylene and a small quantity of marsh-gas, when an electric arc is passed between two carbons in an atmosphere of hydrogen. Of all the many compounds consisting of only carbon and hydrogen these are the only ones which can be obtained by direct synthesis. Under analogous conditions carbon unites with chlorine to form perchloroethane, C_2Cl_6, and hexachlorobenzene, C_6Cl_6.

Oxygen unites with carbon at an elevated temperature to form carbon monoxide, CO, or carbon dioxide, CO_2, according as carbon or oxygen is in excess. If sulphur vapor is passed over red-hot coals, carbon disulphide, CS_2, is produced.

The elements of the nitrogen group, N, P, As, Sb and Bi, do not combine with carbon directly. Silicon and carbon unite at the temperature of the electric furnace to form CSi, *carborundum*, which is so hard that it can be used as a powder for polishing glass and precious stones.

MOISSAN also found that many metals are able to combine with carbon at a very high temperature, forming *carbides*. This was previously known to be true of iron and certain other metals.

The difference in the behavior of these carbides towards water is interesting. Iron carbide is unaffected by it; calcium carbide gives acetylene, C_2H_2; aluminium carbide yields methane; other carbides give mixtures of the two hydrocarbons; uranium carbide produces methane and also liquid and solid hydrocarbons.

179. The *atomic weight of carbon* has been determined with great accuracy by DUMAS and STAS. The averages for the different series of experiments, each of which showed little variation, were as follows:

Ratio by weight of carbon to oxygen in carbon dioxide from the combustion of:

Natural graphite.	2.9994:8.0000
Artificial "	2.9995:8.0000
Diamond.	3.0002:8.0000

The ratio of carbon to oxygen in carbon dioxide is thus very close to 3:8. As the specific gravity of carbon dioxide points to a molecular weight of 44 for this gas, it must contain, according to this ratio, 12.00 parts by weight of carbon and 32 parts of oxygen. The formula is therefore C_xO_2. Inasmuch as no carbon compound is known whose molecular weight includes less than 12 parts of carbon, we have CO_2 as the formula; hence the atomic weight of carbon must be **12.00** for $O=16$.

Compounds with Hydrogen.

180. Carbon and hydrogen form a very large number of compounds (*hydrocarbons*), which are more fully discussed in organic chemistry. Two of them will be treated here briefly.

Methane, also called *marsh-gas* and *fire-damp*, is the only hydrocarbon with just one atom of carbon. It occurs in nature in volcanic gases; moreover, it gushes out of the ground in the neighborhood of the oil-wells at Baku and various places in America. It is an important constituent of "natural gas." It owes the name "marsh-gas" to the fact that it arises from swamps, especially when the decaying vegetation at the bottom is stirred up. It is called "fire-damp" because it occurs in coal beds (§ 177), from which it escapes when they are broken up. It forms a violently explosive mixture with air, which is frequently the cause of mine explosions. For its modes of formation and its physical and chemical properties reference should be had to ORG. CHEM., § 29.

Acetylene, C_2H_2, is a colorless gas of a disagreeable odor. It is soluble in an equal volume of water at 18° and becomes liquid at 18° under 83 atmospheres. Its hydrogen atoms are replaceable by metals. It is manufactured by decomposing calcium carbide with water:

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2.$$

Calcium carbide is prepared by heating coke with unslaked lime (CaO) in the electric furnace. The calcium formed by the action of carbon on lime unites with carbon at the high temperature of the furnace to form CaC_2. Acetylene burns with a vivid flame on coming out of a small orifice under pressure. Since it can be prepared from calcium carbide pretty cheaply, it is used rather extensively in small systems for illuminating purposes. When mixed with air and ignited it explodes vehemently; the compounds with metals are also explosive. It is endothermic and can be exploded by fulminating mercury.

The combustion of acetylene is another illustration of the rule of § 137, that reactions are in most cases of a simpler nature than the chemical equations indicate. The equation here is:

$$2C_2H_2+5O_2=4CO_2+2H_2O.$$

According to this equation the combustion should be septimolecular. Bone and Cain proved, however, that the reaction has more than one stage, the first stage being represented by the bimolecular equation:

$$C_2H_2+O_2=2CO+H_2;$$

CO and H_2 then burn further to CO_2 and H_2O.

From a kinetic standpoint, it is quite conceivable that polymolecular reactions should be rare, for the probability of a large number of molecules coming together in just such a way that a reaction can take place is indeed very slight. The reaction is more likely to proceed in a way which involves the interaction of only very few molecules.

Compounds with the Halogens.

181. Of these we shall mention only **carbon tetrachloride,** CCl_4, which is obtained among other ways by the continued action of chlorine on methane. It is a stable compound, a liquid with an odor like chloroform. Boiling-point 76°. Sp. g. = 1.593 at 20°.

At ordinary temperatures it is not attacked by water; however, when the two are heated together at 250° in a sealed tube, carbon dioxide and hydrochloric acid are formed. Carbon tetrachloride is coming into use as a non-inflammable substitute for benzine in removing grease stains.

Compounds with Oxygen.

Two oxygen compounds of carbon are known: *carbon monoxide*, CO, and *carbon dioxide*, CO_2.

CARBON MONOXIDE, CO.

182. This gaseous compound is always formed when carbon burns in a limited supply of air or oxygen. A number of carbon compounds also yield carbon monoxide when burned under this same condition. It can also be obtained by the action of carbon on oxygen compounds, e.g. by heating zinc oxide, ZnO, with carbon. On passing steam over red-hot coals a mixture of hydrogen and carbon monoxide is produced:

$$C+H_2O=CO+H_2.$$

This mixture goes by the name of *water-gas*. It is used on a large scale for heating and lighting, especially in America. For the latter purpose it is charged with the vapor of hydrocarbons rich in carbon, since its own flame is not luminous. The use of the incandescent gas-light (§ 291) makes this "carburetting" unnecessary. Water-gas containing 50% of carbon monoxide is very poisonous (ORG. CHEM. §415, 2).

Carbon monoxide is also formed by the reduction of carbon dioxide with red-hot carbon:

$$C+CO_2=2CO.$$

This reaction is limited by the reverse one and we have here a case of balanced action expressed by

$$C+CO_2 \rightleftarrows 2CO.$$

In view of the caloric effect of the reaction,

$$2CO=C+CO_2+3900 \text{ Cal.},$$

an elevation of temperature must, according to LE CHATELIER'S rule (§ 51), increase the amount of carbon monoxide; a depression of temperature, the opposite. Experience has shown this to be actually the case. As the temperature rises the quantity of carbon monoxide increases rapidly and at 1000° there is still a very small amount of dioxide. At 445°, on the other hand, practically all the carbon monoxide is changed into carbon dioxide and carbon. This result is surprising, because the same change should also occur at lower temperatures; nevertheless, carbon monoxide seems perfectly stable at ordinary temperatures, even as high as 200°. The cause of this phenomenon must, as in analogous cases, be sought in the very great retardation of the velocity of the reaction $2CO \rightarrow CO_2 + C$ when the temperature sinks. On using certain catalyzers, e.g. finely divided nickel, the velocity of the reaction $2CO \rightarrow CO_2 + C$ becomes measurable as low as 256°.

These measurements have shown that the decomposition of carbon monoxide into carbon dioxide and carbon is not a bimolecular reaction, as would be expected from the above equation, but a unimolecular one. To explain this it may be suggested that the decomposition takes place in two stages: I. $CO = C + O$; II. $CO + O = CO_2$. If we assume that the second stage has an infinite velocity, it is only the first that is really measured, i.e. a unimolecular reaction.

The reduction of salts of carbonic acid also furnishes a method of preparing carbon monoxide. If chalk ($CaCO_3$) or magnesite ($MgCO_3$) is heated with zinc dust, pure carbon monoxide is formed:

$$CaCO_3 + Zn = CaO + ZnO + CO.$$

Physical Properties.—Carbon monoxide is a colorless, odorless gas of a specific gravity of 0.967 (air = 1). It is hard to condense, its critical temperature being −139.5° and its critical pressure 35.5 atmospheres. It boils at −190° and solidifies at −211°. It is only slightly soluble in water.

183. *Chemical Properties.*—Carbon monoxide burns with a characteristic blue flame to carbon dioxide. It can unite with chlorine directly to form *phosgene*, $COCl_2$, and also with sulphur (at an elevated temperature) to form *carbon oxysulphide*, COS, both compounds are gaseous. Again, it unites directly with nickel and iron, giving the compounds $Ni(CO)_4$ and $Fe(CO)_5$ (§§ 214 and 311).

On account of its tendency to combine with oxygen, it displays strong reducing power, especially at high temperatures. Thus metallic oxides, like Fe_2O_3, CuO, etc., are easily converted into the metals when hot. Some compounds are reduced by carbon monoxide even at ordinary temperatures. Palladium is precipitated from an aqueous solution of palladious chloride and an ammoniacal silver solution (prepared by dissolving silver oxide in ammonium hydroxide to the point of saturation) is turned black by the gas on account of formation of the metal. Both of these reactions serve for the detection of carbon monoxide.

An ammoniacal cuprous chloride solution absorbs the gas because of the formation of a compound, $Cu_2Cl_2 \cdot CO + 2H_2O$, which can be isolated in the crystalline state but decomposes again very readily.

The *composition* of carbon monoxide can be determined by exploding a mixture of the gas with oxygen. It is then found that 2 vols. CO unite with 1 vol. O_2 to form 2 vols. CO_2. This together with the vapor density establishes the formula as CO.

CARBON DIOXIDE, CARBONIC ACID ANHYDRIDE, CO_2.

184. This compound occurs not only by itself but also in combination. It is a regular constituent of the air (§ 106); many mineral waters contain the free gas; in some places of the earth (in the Dog's Grotto at Naples and the famous Poison Valley in Java) it comes up out of the ground and it is also found in volcanic exhalations. The most minerals and rocks contain numerous extremely small cavities, partly filled with liquid carbon dioxide. Combined, it occurs in large quantity in the carbonates of lime and magnesia (§ 176).

Carbon dioxide results from the combustion of carbon in an excess of oxygen and also from the direct decomposition of many salts of carbonic acid (*carbonates*) by heat:

$$\underset{\text{Sodium bi-carbonate.}}{2NaHCO_3} = Na_2CO_3 + H_2O + CO_2; \quad CaCO_3 = CaO + CO_2.$$

Moreover, it is formed when a carbonate is decomposed by an acid:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$

By the action of oxygen at high temperatures all carbon compounds are burned with the formation of carbon dioxide. It is also produced by the action of carbon on oxygen compounds, e.g. by heating powdered charcoal with an excess of copper oxide; finally also by the interaction of carbon compounds and oxygen compounds. This latter action is the basis of the general method for determining the proportion of carbon in organic substances; they are heated together with copper oxide and the carbon dioxide formed is absorbed in a weighed amount of caustic potash.

Physical Properties.—Carbon dioxide at ordinary temperatures and pressures is a gas with a somewhat pungent odor and taste. Sp. g. = 1.529 (air = 1). It is thus about half again as heavy as air, so that in those places where it comes out of the earth, as in the Dog's Grotto at Naples, it stays in a layer close to the ground and a dog, for instance, is suffocated while a man can breathe with comfort. Carbon dioxide is easily condensed, becoming liquid at 0° under 35 atmospheres pressure. Its critical temperature is 31.35° and its critical pressure 72.9 atm. Liquid carbon dioxide (" liquid carbonic acid ") is manufactured in great quantities and brought on to the market in steel bottles (bombs). It is a very mobile liquid, which is not miscible with water in all proportions. If the liquid is allowed to escape from the bomb into a coarse linen bag (by inverting the bomb and opening the valve), part of it vaporizes, absorbing hereby so much heat that the remainder solidifies in white flakes. A mixture of this solid carbon dioxide with ether, alcohol or acetone is often used as a freezing-mixture; it enables us to obtain a temperature of −80°, and even −140° *in vacuo*. When liquid carbon dioxide is cooled down in a sealed tube, it congeals to an icy mass, which melts at −65°.

At 15° carbonic acid gas dissolves in its own volume of water (more accurately 1.0020 vol.); at 0° in 1.7967 vol. In alcohol it is still more soluble.

Chemical Properties.—Carbon dioxide is a very stable compound; it is only decomposed by intense heat (see § 182) or by the continued action of induction sparks, breaking up into oxygen and carbon monoxide. This decomposition never completes itself, for just so soon as a certain amount of these gases have been formed, they reunite with explosion. At the moment before the explosion the amount of carbon dioxide still present becomes no longer sufficient to dilute the mixture of oxygen and monoxide enough to hinder an explosion; the *explosive limit* is reached.

Carbon dioxide cannot be farther oxidized; it is therefore not combustible. In general it cannot support combustion either. There are, however, certain substances that take up oxygen from it when hot; if carbon dioxide is mixed with hydrogen and passed through a red-hot tube, carbon monoxide and water are formed; when led over glowing carbon or when heated with phosphorus it is reduced to carbon monoxide. If a burning magnesium ribbon is lowered into carbon dioxide, the oxide of the metal is formed and free carbon is deposited; the same thing happens when sodium or potassium is heated in dry carbon dioxide.

The aqueous solution of carbon dioxide reacts slightly acid; it is supposed that this solution contains a compound H_2CO_3, of which many salts are known. This acid, *carbonic acid*, has not yet been isolated in the free state, however, since it gives off gaseous carbon dioxide ("carbonic acid gas") when its solution is boiled or frozen. If its salts (carbonates) are treated with an acid, no H_2CO_3 is obtained either, for it breaks up forthwith into water and carbon dioxide. Carbonic acid is a very weak acid; it is liberated from its salts by almost every other acid. By adding hydrochloric acid to a carbonate $H^{\cdot}$ ions are introduced into the liquid and they unite with the CO_3'' ions to form integral H_2CO_3 molecules. These, however, break up largely into water and carbon dioxide, the latter of which can only remain in solution up to a certain amount at a constant pressure, so that all in excess of this passes out. As a result the concentration of the H_2CO_3 molecules cannot exceed a definite and, in this case low limit. Since, however, the ionization of these molecules is very weak, in reality all of the carbonate is decomposed by the strong acid (§ 73).

The neutral carbonates of the alkalies are soluble in water, giving an alkaline reaction, as a result of partial hydrolysis (§ 66). The acid, H_2CO_3, is a weak acid, although its salts, e.g. K_2CO_3, are strong electrolytes. A solution of such a salt, therefore, contains a large number of CO_3'' ions, part of which must unite with the $H^{\cdot}$ ions of the water in order to establish the equilibrium between carbonic acid and its ions. The result of this is that other molecules of water must be split up into ions in order to compensate the loss of $H^{\cdot}$ ions. This leaves in the liquid a certain number of OH' ions, which are not balanced by an equal number of $H^{\cdot}$ ions. The liquid therefore acquires an alkaline reaction.

The carbonates of the other metals are insoluble in water; however, the acid carbonates are mostly soluble. Calcium carbonate, e.g., dissolves in water containing carbonic acid. The solutions of such acid carbonates give off carbon dioxide on merely boiling, however, and the neutral carbonates are precipitated. In the solid state also the acid carbonates give off carbonic acid gas very readily on warming.

Composition of Carbon Dioxide.—In connection with what was stated in § 179 it is an important fact that no change of volume occurs when carbon burns in an excess of oxygen:

$$C + \underset{\text{1 vol.}}{O_2} = \underset{\text{1 vol.}}{CO_2}.$$

Still higher oxygen compounds of carbon are known, of which **percarbonic acid** may be mentioned here. It has been prepared in the form of a salt, **potassium percarbonate,** $K_2C_2O_6$. The latter is produced by the electrolysis of a saturated potash solution at −15°; this synthesis may be considered as analogous to that of persulphuric acid (§ 91). Here the potash is split up in $K^{\cdot}$ and KCO_3'; the latter ions are discharged at the anode and two of them unite to form $K_2C_2O_6$. It separates out as a sky-blue precipitate, which after being dried in a phosphorus pentoxide desiccator is a light-blue powder consisting of K_2CO_3 and $K_2C_2O_6$. Even gentle warming decomposes the percarbonate:

$$K_2C_2O_6 = K_2CO_3 + CO_2 + O.$$

It acts therefore as a strong oxidizing-agent; it oxidizes lead sulphide to the sulphate, bleaches indigo, etc. Manganese dioxide and lead peroxide are converted into the respective carbonates in a vigorous reaction, in which case it acts as a reducing-agent.

Other Carbon Compounds.

185. **Cyanogen,** $(CN)_2$, can be prepared by heating mercuric cyanide, $Hg(CN)_2$, or by treating a solution of potassium cyanide with copper sulphate solution. It is possible that first cupric cyanide is formed and that this at once breaks up into cuprous cyanide and cyanogen:

$$4KCN + 2CuSO_4 = 2K_2SO_4 + Cu_2(CN)_2 + (CN)_2.$$

Cyanogen has a penetrating odor. When liquefied it boils at −20.7°. It is unaffected by high temperatures. It dissolves in water, but the solution deposits amorphous brown flakes after a while. It burns with a purple-tinged flame according to the equation

$$C_2N_2 + 2O_2 = 2CO_2 + N_2.$$

The reaction, however, is not trimolecular, the first stage being

$$C_2N_2 + O_2 = 2CO + N_2.$$

i.e. a bimolecular process.

This was proved by DIXON by determining the velocity of propagation of the explosion of mixtures of cyanogen and oxygen. When explosive gas mixtures are introduced into a long tube and their explosion started at one end (by an electric spark, for example) a flame results, which is propagated through the tube with a definite and measurable velocity. BERTHELOT called this self-propagating flame the *explosion wave.*

DIXON ignited a mixture of 1 vol. cyanogen and 1 vol. oxygen, obtaining after the explosion carbon monoxide and nitrogen; the velocity of the explosion wave was found to be 2728 m. per sec. Thereupon he mixed 1 vol. cyanogen with 2 vols. oxygen in one instance and with 1 vol. oxygen and 1 vol. of an indifferent gas in another instance; in both cases the velocity of the explosion wave was nearly the same, viz. 2321 m. and 2398 m. per sec. It is plain, therefore, that the second volume of oxygen influenced the explosion wave in the same way as the indifferent gas, viz. as a diluent. The conclusion may be drawn that in the explosion wave itself only carbon monoxide and nitrogen are formed, even in the presence of an excess of oxygen. However, since the tube contains only carbon dioxide and nitrogen after the combustion, it must be assumed that the combustion of carbon monoxide to carbon dioxide is a secondary process.

In its chemical behavior cyanogen displays an analogy with the halogens. Potassium burns in it as in chlorine, forming *potassium cyanide,* KCN. If cyanogen is passed into potassium hydroxide solution, the same cyanide is formed together with *potassium cyanate,* KCNO, analogous to the formation of the chloride and hypochlorite, KCl and KClO, on leading chlorine into potassium hydroxide (§ 56). *Silver cyanide* is curdy, insoluble in water and dilute acids and soluble in ammonia, like silver chloride.

Hydrogen cyanide, HCN (*prussic acid*), is important in inorganic chemistry because of the numerous complex salts which it forms. Those of the alkalies are soluble in water and crystallize beautifully; see § 308. The salts of the alkaline earths and mercuric cyanide are also soluble in water, the other salts insoluble.

The Flame.

186. A flame is produced by the burning of a gas; solids, like iron, carbon, etc., burn without a flame. If a flame is observed during the burning of mineral coal, a candle or the like, it is due to the fact that at that high temperature gaseous decomposition-products are formed, which burn. If a gas burns in the air, it is called a combustible gas and the oxygen of the air is called the supporter of the combustion. These expressions in common use are only relative terms; it is possible to light the oxygen and have it burn with a flame in a gas which is ordinarily called combustible. This phenomenon is illustrated in a way by the *reverse flame.*

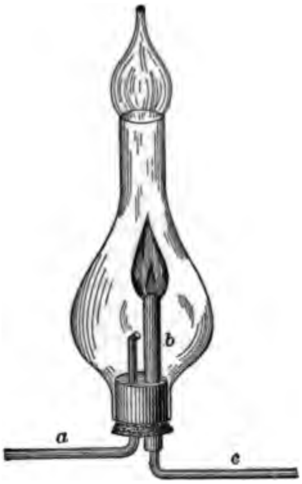


FIG. 46.—REVERSE FLAME.

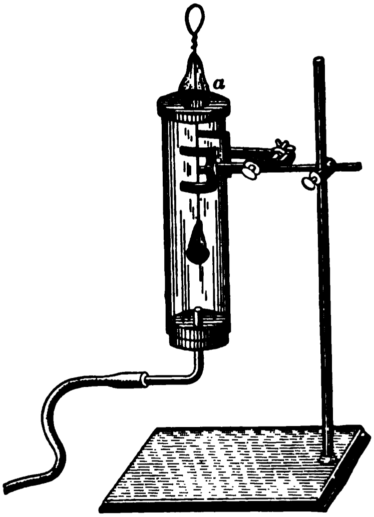


FIG. 47.—POTASSIUM CHLORATE FLAME.

This can be easily obtained with the aid of the apparatus of Fig. 46. A lamp-chimney is fitted with a two-hole cork at its lower end. Through the narrower hole of the cork a small tube *a* is inserted for conducting in the gas; through the wider hole a tube *b* for the admission of air. The chimney is first removed and the gas coming out of tube *a* lighted and so regulated as to produce a small flame. Then the chimney is replaced; the flame continues to burn quietly, inasmuch as plenty of air is supplied by the wider tube. Thereupon the gas supply is gradually increased and at a certain moment the small flame at the end of *a* is extinguished and a large pale flame appears at the end of *b*; it is air burning in the gas which fills the chimney. This is the reverse flame of air in illuminating-gas. At the same time the excess of gas escaping at the top ignites in the outside air, so that the apparatus presents both a direct and a reverse flame at the same time. That it is really air that burns at the mouth of *b* is proved by introducing a tiny gas-flame by means of the tube *c* into the flame of the wide tube *b*; the small flame continues to burn.

Substances that give up oxygen are capable of burning when surrounded by a combustible gas. The experiment can be carried out with potassium chlorate as follows: Illuminating-gas is conducted into a glass cylinder (Fig. 47) and lighted at the top, where the cylinder is covered by a thin piece of metal with a hole in it. A little potassium chlorate is then lowered into the flame by means of a deflagrating spoon and heated till oxygen comes off freely. If the bowl is then dipped down in the cylinder, the oxygen burns with a very luminous flame, which is colored violet-blue by the vaporization of some potassium salt.

We saw above (§ 27) that a hydrogen flame continues to burn in chlorine with the formation of hydrochloric acid; on the other hand chlorine can also be made to burn in hydrogen. For this purpose a cylinder closed at the top is filled with hydrogen and lit at the lower edge. A tube through which chlorine is supplied is then brought in contact with this flame and inserted in the cylinder. The chlorine burns on.

187. A flame may be luminous or non-luminous. It gives light when solid particles are suspended in it. An ordinary gas-flame is luminous because particles of carbon, set free by the combustion, are made to glow. On introducing a cold object into the flame they are deposited as soot. The light of the WELSBACH *incandescent gas-light* is produced by the glowing incombustible mantle (§ 291).

Such flames give a continous spectrum (§ 263). Many gases, which yield only gaseous products on burning, give either a very faint light or none at all, e.g. hydrogen, carbon monoxide, etc. However, when hydrogen burns in oxygen of 20 atmospheres pressure, its flame is strongly luminous. Other incandescent gases, such as the vapors of certain metals, can render a flame luminous even at ordinary pressure, imparting to it a definite color. Colored flames of this sort give a line spectrum (§ 263).

A gas-flame, whose light is due to incandescent particles of carbon, is made non-luminous by mixing the gas with air before the combustion. This is the principle of the BUNSEN burner (Fig. 48) which is used in all laboratories and quite extensively also, with some variation or other, in heating and cooking apparatuses (gas stoves).

The Bunsen burner consists of a base in which is a tube for supplying the gas, which escapes from a narrow orifice at *a*. Here it mixes with air that enters through the lateral holes in *c*, the proportion of air being regulated by the collar *b*. This mixture burns with a colorless flame when ignited at the top of *c*.

The opinion was originally held that the loss of luminosity of the flame is due to the *oxygen* of the air, the latter causing the complete combustion of the carbon particles. As has since been shown, however, the dilution of the burning gas with nitrogen also has a part in it: if illuminating-gas is mixed with two or three times as much nitrogen, the former burns with a colorless flame.

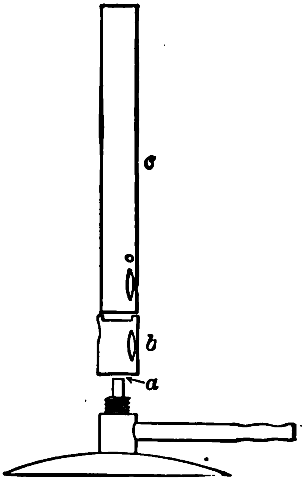


FIG. 48.—BUNSEN BURNER.

With the aid of a wire gauze a burning gas mixture can be cooled so low that the combustion cannot propagate itself through the gauze; in other words, the flame does not get through the gauze (Fig. 49.). If gas is allowed to flow out of a BUNSEN burner and a wire gauze is held across the current a short distance from the orifice, the gas can be lit above the gauze without the flame springing back to the burner.

It was by experiments such as these that DAVY was led to discover his *miner's safety-lamp*. As Fig. 50 shows, this consists of an oil-lamp, the flame of which is surrounded by a wire cage. A combustible gas mixture may catch fire inside of the lantern, but the fire cannot pass through the gauze to the outside.

188. The *temperature of the flame* is much lower than we might suppose. Since, when hydrogen burns in oxygen, 57.2 kg.-calories are produced by every 18 g. of the mixture, and the specific heat of steam is 0.48, this amount of heat ought to raise the 18 g. steam to a temperature of $\frac{57.2}{0.018\times0.48}=6600°$. In reality the temperature of the flame does not exceed 2500°. This difference between calculation and observation is due to the fact that on account of dissociation only a partial combination of hydrogen and oxygen takes place in any part of the flame. The temperature of 6600° could indeed be obtained at any point, if the gases united there completely and instantaneously; but this is impossible, for above 1300° the formation of the compound is checked by the opposite process, the dissociation of steam. Therefore what occurs must be this: oxygen and hydrogen, when brought together at the aperture, combine and effect a certain rise of temperature; in the same measure as the system in equilibrium (hydrogen, oxygen, steam) cools off, fresh portions of the gases unite. Their combustion cannot therefore take place at any particular point but must be gradual throughout the whole extent of the flame and at any one point the temperature cannot exceed a certain limit, which is determined by the degree of dissociation of the combustion product.

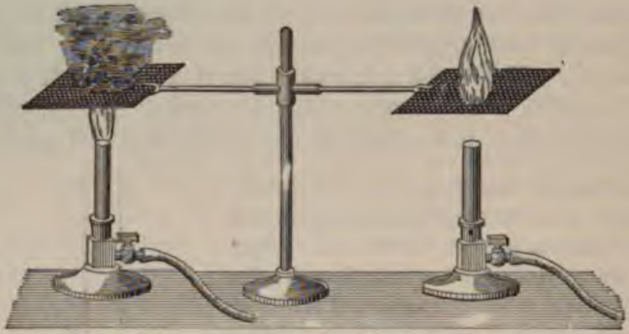


FIG. 49.—EFFECT OF A WIRE GAUZE ON A FLAME.

FIG. 50.—MINER'S SAFETY-LAMP.

189. ***Zones of a luminous flame.*** Let us take a candle-flame, for example. In the central zone (1 in the diagram Fig. 51)

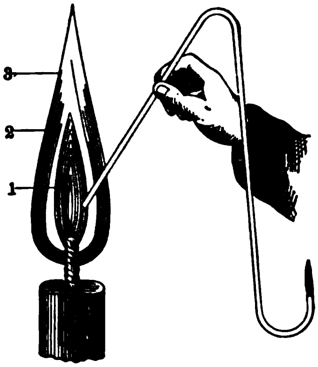


FIG. 51.—ZONES OF A LUMINOUS FLAME.

there is no combustion. The stearin of the candle is here converted by the heat of the flame into volatile combustible products. In a large candle this can be proved in the manner shown in Fig. 51. The narrow tube conducts off the inflammable gases and they can be lit at the outer end.

The hollowness of a flame can be demonstrated in various ways; in a Bunsen burner, for instance, by placing a match-head in the center, where it does not ignite, or by holding a thin platinum wire across a flame; the wire only glows at the edges of the flame.

The dark central zone of the flame is next surrounded by the luminous zone (2). Here the volatilized hydrocarbon is decomposed with the separation of carbon, because the air supply is insufficient for complete combustion. These carbon particles become incandescent and so make the flame luminous. Finally there is the blue outer zone (3), in which the glowing particles of carbon are burned by direct contact with the air. It radiates very little light.

The amount of solid carbon in a flame which is raised to incandescence and hence gives light is very small, as the following calculation shows. The substances in burning illuminating-gas which break up with the liberation of carbon are chiefly benzene and ethylene. The former makes up about 1, the latter about 4, per cent by volume of the gas. If we assume that the benzene is completely broken up and the ethylene only half, then the total amount of carbon deposited by 1 liter of burning illuminating-gas is about 54 mg. The volume of the luminous part of a gas flame with a consumption of 150 liters per hour amounts to about 2 c.c. (reduced to 0°), so that the mass of solid incandescent carbon present in it is only $\frac{2\times 54}{1000}=0.1$ mg.

SILICON.

90. This element in combination with oxygen is one of the principal constituents of the earth's crust (§ 8). In the free state, however, it does not occur in nature, being found almost exclusively as *silica*, SiO_2, or in the *silicates*. Sand and the many varieties of quartz are different forms of natural silicon dioxide; the number of silicates is very large.

Free silicon is obtained by heating sodium fluosilicate, Na_2SiF_6, with sodium:

$$Na_2SiF_6+4Na=6NaF+Si,$$

or by heating sodium in an atmosphere of silicon tetrafluoride:

$$4Na+SiF_4=4NaF+Si.$$

The sodium fluoride can be removed by water.

Another method, which is far easier, is to mix 400 g. aluminium filings with 500 g. sulphur and 360 g. sand. This mixture is ignited, whereupon it burns with a large flame. The mass fuses and becomes white-hot. When cooled it consists principally of aluminium sulphide and free silicon. It is then treated with dilute hydrochloric acid, which decomposes and dissolves the sulphide, leaving the silicon behind. (KÜHNE method.)

Allotropic Forms.—The silicon obtained by the two first-named methods is a brown amorphous powder; it can be fused under a layer of molten sodium chloride and obtained crystalline on cooling. The latter form is best prepared by KÜHNE'S method. The crystals are regular, black, and of a high lustre. If silicon is heated in the electric furnace, it vaporizes and condenses again in small globules, mixed with a little gray powder and some silica.

Chemical Properties.—Silicon takes fire only when heated in the air to a very high temperature, burning to silica. It unites with fluorine at ordinary temperatures, the combustion being marked by a glow; combination with chlorine takes place on gently warming. At an elevated temperature silicon combines with nitrogen and some metals; these *silicides* have been prepared mainly by MOISSAN in his electric furnace.

It is indifferent towards sulphuric, nitric and hydrochloric acids. Hydrofluoric acid dissolves it, however, with the evolution of hydrogen. Hydrogen chloride gas reacts with it at a high temperature, forming silicon tetrachloride and silico-chloroform. It dissolves in a hot solution of sodium or potassium hydroxide, producing hydrogen and a silicate:

$$Si+2KOH+H_2O=K_2SiO_3+2H_2.$$

Hydrogen Silicide, SiH_4.

191. This gas is obtained by adding freshly prepared magnesium silicide to hydrochloric acid. The magnesium silicide is prepared by heating sand with an excess of magnesium powder, or better by fusing 40 parts of anhydrous magnesium chloride with a mixture of 35 parts of sodium fluosilicate, 10 of sodium chloride and 20 of sodium. The hydrogen silicide so obtained is mixed with hydrogen. A purer product results from heating an organic derivative of silicon, tri-ethyl silicoformate:

$$4SiH(OC_2H_5)_3=3Si(OC_2H_5)_4+SiH_4.$$

Hydrogen silicide, or silicon tetrahydride, is a gas, which becomes liquid at −1° under a pressure of 100 atmospheres. It has a disagreeable odor. It takes fire in the air; each bubble that escapes from the generator forms a cloudy ring of hydrated silica. If, however the hydrogen silicide is perfectly pure, it does not ignite spontaneously in the air at ordinary temperatures except under reduced pressure. MOISSAN has found that in the decomposition of magnesium silicide, Mg_2Si, by hydrochloric acid there is also formed a small quantity of *silico-ethane*, Si_2H_6, a liquid boiling at 52°. It ignites spontaneously in the air and is the cause of hydrogen silicide taking fire in the air, even at ordinary pressure. We have therefore in this case phenomena similar to those in the case of hydrogen phosphide (§ 137). Heat decomposes the hydrogen silicide readily into Si and $2H_2$. It burns in a chlorine atmosphere and is decomposed by an alkali solution according to the equation:

$$SiH_4+2KOH+H_2O=4H_2+K_2SiO_3.$$

Halogen Compounds of Silicon.

192. **Silicon tetrachloride,** $SiCl_4$, is prepared by heating silicon in a current of chlorine at 300°-310°. It is a liquid with the specific gravity 1.5241 at 0° and the boiling-point 59.6°. It is instantly decomposed by water, forming hydrochloric acid and hydrated silica.

Silico-chloroform, $SiCl_3H$, is obtained, together with a large quantity of silicon tetrachloride, on heating silicon in a current of hydrochloric acid gas (§ 190 . From this mixture it is separated by fractional distillation. It is a colorless, strongly smelling compound, which fumes in the air, boils at 34° and is decomposed by water.

Silicon tetrafluoride, SiF_4, can be obtained by warming a mixture of sand and calcium fluoride with concentrated sulphuric acid:

$$2CaF_2+SiO_2+2H_2SO_4=SiF_4+2CaSO_4+2H_2O.$$

It is a colorless gas with a very pungent and suffocating odor; it condenses under 9 atm. pressure or by cooling to $-160°$. When perfectly dry, it does not attack glass.

Silicon fluoride is also formed by the action of hydrogen fluoride on silicates; the silica is first set free from them and then attacked in the way just described. Glass-etching (§ 53) depends on this action.

By the repeated treatment of silicates with hydrous hydrofluoric acid all the silicic acid is driven off as silicon fluoride. The bases which were in combination with the silicic acid are left behind in the form of fluorides. They can be transformed into sulphates by warming with sulphuric acid and then converted into a form suitable for *analysis*. We have here a very useful means of determining the metals present in the silicates.

Water decomposes silicon fluoride as follows:

$$3SiF_4+3H_2O=H_2SiO_3+2H_2SiF_6.$$

The compound H_2SiF_6 is called **hydrofluosilicic acid;** it is known only in aqueous solution. If the latter is concentrated by evaporation, silicon tetrafluoride escapes but hydrogen fluoride stays in solution. When the concentration corresponds to 13.3% H_2SiF_6 the vapor contains 2HF to $1SiF_4$; but dilute solutions yield a vapor which contains much more hydrogen fluoride. If, therefore, a concentrated solution of hydrofluosilicic acid is partially evaporated, the residual liquid is able to dissolve silica because of the presence of free hydrofluoric acid. On the other hand, a dilute solution, after partial evaporation, leaves a residue, from which silicic acid is deposited, because the excess of silicon tetrafluoride which it contains is decomposed by water according to the above equation.

The decomposition of silicon fluoride by water is usually demonstrated in the following way: The compound is generated in the prescribed manner in a flask (Fig. 52), whereupon it is conducted through a doubly-bent glass tube into a cylindrical jar containing a little mercury (into which the tube opens) and on top of this some water. Every bubble of gas that rises from the mercury into the water generates in the latter a cloud of silicic acid. If the glass tube opened directly in water, it would soon become stopped up because of this decomposition.

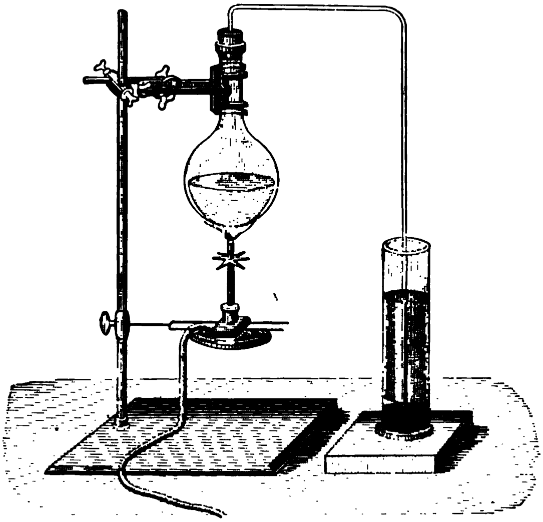


FIG. 52.—PREPARATION OF HYDROFLUOSILICIC ACID.

The solution of hydrofluosilicic acid reacts acid; it dissolves metals with the evolution of hydrogen and behaves in all respects like an acid. A hydrate, $H_2SiF_6+2H_2O$, is known in the solid state. It melts at 19°, and is obtained by leading silicon fluoride into concentrated hydrofluoric acid. Most of the salts of hydrofluosilicic acid are soluble in water; the potassium salt is difficultly so, however, and the barium salt is insoluble.

Hydrofluosilicic acid is used in hardening objects made of gypsum (this is due probably to the formation of calcium fluoride) and also in analytical chemistry.

Oxygen Compounds of Silicon.

193. Only one such compound is known: *silicon dioxide*, or *silica*.

SILICA, SiO_2.

This compound occurs in astonishingly large quantities and in a great number of varieties in the solid crust of the earth. It is found crystallized as *rock crystal*, *quartz* (when colored brown, called *smoky quartz*), *amethyst* (the more beautiful sorts being used for ornament), *tridymite*, *onyx*, *cat's-eye*, etc. Sand is largely silica; sandstone also belongs here and so does *jasper* (usually colored red with ferric oxide and having a conchoidal fracture). *Opal* is an amorphous variety, containing varying amounts of water.

Silica can be prepared artificially as an amorphous white powder by heating silicic acid.

Physical Properties.—In the crystallized state silica is very hard and insoluble in water and has a specific gravity of 2.6. It is very difficultly fusible; in the oxyhydrogen flame it softens and passes over into a vitreous modification. When heated strongly this can be drawn out into extremely fine threads that are so tenacious and display so regular a torsion that they are frequently used in suspending magnets, etc., in physical instruments. It can be made to boil vigorously in the electric furnace; the vapor condenses in woolly flakes. Quartz that has been fused has a very small coefficient of expansion (about $^1/_{17}$ of that of platinum); this explains why objects made of it can endure very sudden changes of temperature. They can be heated very hot and then thrust into cold water at once without cracking. They are attacked only by metallic oxides and at a high temperature. Recently it has become possible to utilize fused (vitreous) quartz for the manufacture of chemical apparatus.

Chemical Properties.—Especially in the crystallized condition silica is very little acted upon by acids except hydrofluoric acid (§ 193). Fused alkalies dissolve it, forming alkali silicates. It can be reduced by carbon in the electric furnace, carborundum (§ 178) being formed. It is also reduced by heating with magnesium (§ 190).

Silicic Acids.

194. When a solution of potassium or sodium silicate (*water-glass*) is treated with hydrochloric acid, a very voluminous, gelatinous mass separates out; this consists of hydrous silicic acid corresponding to the general formula SiO_2aq. After being washed with water and dried in the air it is a fine white amorphous powder of the approximate composition H_2SiO_3. Freshly precipitated silicic acid is slightly soluble in water, but more so in dilute hydrochloric acid If, therefore, water-glass is introduced into an excess of hydrochloric acid, the silicic acid stays in solution; it can be separated from the sodium chloride simultaneously formed, by the following process:

The solution is put into a piece of parchment tubing, which is tied at both ends, and the whole submerged in pure water, the latter being frequently renewed. It is found that the salt goes through the parchment, but that the silicic acid does not. This process is called **dialysis** and any arrangement for carrying it out is known as a *dialyzer*. GRAHAM found that crystallizable substances in solution (*crystalloids*) are able to pass through such a membrane, while other substances, which he called *colloids*, are not. In the latter class are glue, gums, gelatine, albumen—in short, many amorphous substances occurring in the animal and vegetable kingdoms. Purification by dialysis is also possible with certain inorganic substances besides silicic acid.

A pure solution of silicic acid—a so-called *colloidal* solution—is obtained only by a long process of dialysis (five or six weeks). It then contains but little silicic acid, part of the latter having passed gradually through the membrane. It can be concentrated by careful evaporation, but when the amount of acid reaches about 1½% it coagulates. If a small amount of alkali or hydrochloric acid is added, the solution of silicic acid can be obtained much stronger (as high as 12%) without coagulating. The silicic acid which separates from the colloidal solution dries in the air to a white amorphous powder, still containing a good deal of water, however. The water can be slowly extracted in a sulphuric acid desiccator.

Since silicon tetrachloride is changed to silicic acid by water, just like phosphorus pentachloride to phosphoric acid (§ 145), we can consider the compound as the basis from which the remaining silicic acids are derived. The latter can in general be represented by the formula $m\mathrm{Si(OH)_4}-n\mathrm{H_2O}$.

These **polysilicic acids** themselves have not been isolated, but many of their salts and double-salts are known, which occur as minerals in nature. It is a striking fact that, while the great ability of the carbon atom to combine with other carbon atoms is the foundation of the organic world, the quadrivalent element silicon, so closely allied to carbon, is by reason of its ability to form complex silicates the basis of a very extensive part of the inorganic world.

The silicates of potassium and sodium are soluble in water, those of the other metals insoluble, as are also most of the double silicates of the alkalies.

In the soil hydrous silicates are found whose bases are usually lime and alumina. In contact with alkali salts these undergo a double decomposition, an insoluble potassium aluminium silicate, for example, being formed together with chloride of calcium, which is taken off by the underground water. This phenomenon is said to be caused by the *absorptive power* of the soil; it plays an important rôle in the determination of soil-values. It is this that holds back the potash, an invaluable nutrient, which is furnished to the soil in the form of potassium salts and would otherwise be quickly washed off by the rain because of its solubility.

The soluble phosphates are "absorbed" by the soil in the same way. This is mainly to be ascribed to the lime they contain, with which insoluble tri- or dicalcium phosphate is formed; to some extent this absorption may be caused also by basic lime silicates.

Silicon Compounds of Other Elements.

195. Silicon sulphide, SiS_2, is produced when carbon disulphide vapor is led over a mixture of charcoal and silica at red heat. It forms long, silken needles, which are broken up by water into SiO_2 aq and hydrogen sulphide.

Silicon nitride, Si_2N_3, a white amorphous substance, results from the heating of silicon in an atmosphere of nitrogen. (For metal silicides *cf.* § 190.)

COLLOIDS.

196. In silicic acid we have become acquainted with a substance that occurs in a special form, viz. as a colloid. A considerable number of such substances is now known, and the study of them has latterly been so active and prolific that a brief recapitulation of the principal results is fitting at this point. The colloids comprise among other substances the *agglutinants,* as they are called,—gelatine, agar-agar, albumins, starch, etc. When they are mixed with water they swell up and on being gently warmed form a solution. When cooled they *gelatinize,* i.e. they congeal to a soft, viscous mass, which retains all the solvent water. The solution itself is called a **hydrosol** (or, in case alcohol is the solvent, an *alcosol*) and the gelatinized mass a **hydrogel.**

When the solvent water is extracted from a hydrosol by evaporation at a low temperature a hydrogel is at first formed, which still contains a great deal of water. This water is partially lost on exposure to the air,—more rapidly in a desiccator,—and its vapor tension does not differ perceptibly from that of pure water. When, however, a certain stage of dehydration is reached the vapor tension begins to diminish. If water is added to the hydrogel before this stage is reached, a hydrogel is again obtained with the same properties as originally. The process of sol- and gel-formation is thus a reversible one; the hydrosol is therefore called **reversible.**

Other interesting properties are attached to hydrosols. Crystalloid salts, for example, diffuse in them,—even in the congealed mass,—just as easily as in water. If a piece of jellied agar-agar is immersed for some time in a dark blue ammoniacal solution of a copper salt, the agar-agar becomes stained throughout its entire mass. Colloids, on the contrary, do not diffuse.

This can be shown with a colloidal solution of Prussian blue, which does not penetrate at all into the agar-agar, as above. The electrical conductance, too, is practically the same for a gel containing crystalloid salts in solution as for an aqueous solution of the same salts at like concentration.

Oftentimes large amounts of crystalloid salts can be added to a reversible hydrosol without the formation of gel. This is very different with the second class of colloids, the **irreversible** colloids, for they are in many cases very sensitive to additions of salts. When the salt is added the irreversible hydrosol begins to appear cloudy, and a precipitate is formed which cannot be reconverted offhand into hydrosol.

Irreversible hydrosols can be prepared in various ways. Frequently they are formed in place of precipitates when ions are carefully excluded. If, for example, hydrogen sulphide is passed into a solution of arsenic trioxide, there is no precipitation of As_2S_3 but a yellow coloration of the solution, the sulphide being produced in the form of a colloidal solution. The addition of a little hydrochloric acid, a highly ionized substance, suffices to throw out the As_2S_3 as a yellow precipitate. Again, mercuric cyanide is a compound that is hardly ionized at all in aqueous solution. When the very feebly ionized hydrogen sulphide is passed into a $Hg(CN)_2$ solution the resulting mercuric sulphide remains in colloidal solution; however, it separates out if the solution is previously acidulated with a small quantity of a strong mineral acid.

Another method of preparing irreversible colloids is by dialysis, as described in connection with silicic acid. In this way hydrosols of iron oxide, alumina and many other substances can be obtained. Iron oxide hydrosol, for example, is obtained when ferric chloride, $FeCl_3$, is dissolved in water, ammonia is added all but to the point of precipitation and the whole is dialyzed. Ammonium chloride, NH_4Cl, and hydrochloric acid pass through the membrane ($FeCl_3$ is partially hydrolyzed in aqueous solution; see § 66) and $Fe_2O_3 \cdot aq$ remains as a colloid in solution.

A third method is that of comminuting metals under water. Wires of various metals, such as platinum and gold, are connected with the poles of a source of electricity at about 110 volts. On bringing the wires sufficiently close together under water a small arc is produced. The metal then flows off from the cathode into the liquid as a dark cloud of extremely fine particles. After the coarser particles are filtered off a clear, dark solution is obtained, containing the metal as hydrosol. Hydrosols obtained in this way are very mobile liquids; they are precipitated by the addition of slight amounts of electrolyte.

Certain hydrogels like those of silicic and stannic acids are insoluble when pure, but are dissolved by water to form colloids upon the addition of a trace of an electrolyte,—for a tin oxide hydrogel a few drops of diluted ammonia water suffice. GRAHAM called this phenomenon *peptonization*; as a matter of fact the gradual clarification of a turbid hydrogel-water mixture under the influence of the peptonizing-agent greatly resembles an artificial digestion.

The quantity of an electrolyte that is just sufficient to precipitate an irreversible hydrosol is connected with the valence of the electrolyte, the quantity decreasing rapidly with increasing valence. The As_2S_3 hydrosol is just coagulated by 71 mill-equivalents of NaCl per liter, 2.0 of $MgCl_2$ and 0.39 of $AlCl_3$.

Hydrosols that are very sensitive to the presence of electrolytes, notably the hydrosol of gold, can be made stable by the addition of hydrosols of the gelatine type, which are indifferent to electrolytes. It is in this manner that "collargol," a preparation of therapeutic value, is prepared, it being a stabilified silver hydrosol. The added colloids have been termed **protective colloids.**

Certain colloids are capable of mutually precipitating each other; others are not. The hydrosols of ferric oxide and arsenious sulphide give a precipitate when mixed, but the hydrosols of gold and arsenious sulphide mix without precipitation. These phenomena have been shown to be connected with the behavior of the substances toward the electric current. If a solution is introduced into a U-tube supplied with electrodes at the upper ends and a strong current (say 110 volts) is passed through it, the colloid is seen to separate out and wander either to the anode or to the cathode. At one of the two electrodes an aqueous layer appears, which is entirely free from colloid and is separated sharply from the hydrosol. This convective transference, or

electrical endosmose, is by no means to be confused with the ionic migration in electrolytes. For, while in the electrolytes there is an electrical opposition between the dissociation products of the dissolved substance, the electrical opposition exists in this case between the colloid and the solvent. In general, mutual precipitation is only possible with colloids whose electrical charges are oppsoite with respect to that of a common solvent. Many hydrosols are perfectly clear in ordinary daylight and cannot be separated into their constituents by the ordinary mechanical means of separation (filtration, decantation, etc.). Gold hydrosol, for example, looks just like some splendid red solution. Even under a microscope of highest power no floating particles can be detected. Nevertheless a hydrosol is in most cases heterogeneous. The TYNDALL *effect* demonstrates this. When a beam of light passes through a body of air that is free from dust it is invisible transversely; the gas is "optically a vacuum." But, so soon as dust particles enter the air, the path of the beam can be followed through the dispersion of the light by the particles. Optically vacuous liquids and optically vacuous solutions of crystalloid salts can also be prepared. But if a beam of light is passed through a hydrosol the path of the beam can be seen. The hydrosol is therefore not an optical vacuum; it must contain floating particles. SIEDENTOPF and ZSIGMONDY have succeeded in rendering these submicroscopic particles visible with an apparatus that they call the *ultramicroscope*. In it the hydrosol is illuminated transversely so that the luminous rays do not blind the eye of the observer. The submicroscopic particles bend (diffract) the light rays in all directions, so that with sufficiently intense illumination the light effect produced by each individual particle comes within the range of microscopic visibility and can be separately observed without revealing its form.

When very fine pulverulent substances like clay, emery powder, etc., are stirred up in water, the latter often remains turbid for weeks. Such a mixture is called a **suspension.** As the particles become smaller and smaller, the suspension more and more approaches the hydrosol. While suspensions with particles of 1–10μ(μ=0.001 mm.) have an extremely heterogeneous appearance liquids containing particles smaller than 20$\mu\mu$($\mu\mu = 10^{-6}$ mm.) appear clear in ordinary daylight, even when the refractive indices of the medium and the comminuted substances are as different as those of water and metallic gold. We must assume that there is a continuous series of transitions between suspensions and colloids. The incomparably finer division in the case of the colloids is accompanied by a progressive change of properties. These colloids even begin to show the properties of crystalloid solutions. Hydrosols, for example, have an appreciable, though very slight, osmotic pressure and a corresponding slight depression of the freezing-point, also a very small diffusion velocity, etc. These properties are unquestionably due to the enormously increased surface which extremely finely divided substances have in comparison with the coarse powders. The attraction effects between the fine particles and the molecules of the solvent are great enough to come within the range of measurement. This suffices for the explanation of the osmotic pressure, etc. It is now easy to understand how that when the division of matter goes still further than with the colloids, this attraction influence may become of such a magnitude or nature as to develop the properties of real crystalloid solutions. Just as there is an unbroken series of intermediate stages between coarse mechanical suspensions and colloids, so there is a similar bridging over between colloid and crystalloid solution. The recent colloid researches lead us, therefore, to the conclusion that there are no sharp lines of demarcation between suspensions, colloid solutions and crystalloid solutions, and that as matter is carried to a finer and finer state of division, it passes from a suspension to a hydrosol and, finally, to a crystalloid solution.

GERMANIUM.

197. This element is of extremely rare occurrence. It was discovered by WINKLER in an argentiferous mineral, *argyrodite*, $GeS_2 \cdot 4Ag_2S$, found in Freiberg, in Saxony. Germanium forms grayish-white octahedrons with a metallic lustre and a specific gravity of 5.469 at 20°. It melts at 900°. At ordinary temperatures it is unaffected by the air; at red heat it burns, forming white fumes of germanium oxide, GeO_2. Two series of compounds of this element are known, which are derived from the oxides GeO and GeO_2; the *ous* compounds are easily oxidized to the higher form, germanic acid. The hydrogen compounds, GeH_4 and $GeHCl_3$, are known.

Germanic chloride, $GeCl_4$, can be prepared directly from the elements. It is broken up by water forming $Ge(OH)_4$.

Germanium dioxide, GeO_2, is produced by heating the corresponding hydroxide, or by roasting the element or its sulphide or by treating it with nitric acid. It is a white powder of a specific gravity of 4.703 at 18° and is unaffected by heat.

Germanium disulphide, GeS_2, separates as a white precipitate when hydrogen sulphide is passed into the solution of germanium dioxide in strong hydrochloric acid. In moist air it decomposes, giving off hydrogen sulphide. It dissolves in alkalies and alkali sulphides to form sulpho-salts.

For germanium *cf.* also § 218.

TIN.

198. This metal is not very widely distributed on the earth; in some places, however, it is found in quite large quantities. The principal tin mines of Europe are those in Cornwall; even the Phœnicians obtained tin there. The most important present localities are on the group of islands lying east of Sumatra (Banca, Billiton, Sinkop, etc.). There the metal occurs in the form of tinstone (*cassiterite*, SnO_2); it is found in quadratic crystals, which are usually colored brown or black by a small amount of iron. In order to extract the metal, the ore is at first roasted, to eliminate any sulphur or arsenic it may contain, and then reduced with carbon. The tin thus obtained is refined by liquation, i.e. by fusing again at a low temperature and pouring it off from the less fusible alloy of tin with iron and arsenic. It is then melted once more and stirred with a wooden pole (branch of a tree), whereby the oxide still remaining is reduced. The Banca tin is nearly chemically pure.

Physical Properties.—Tin is a silvery-white metal, melting at 232.7° and volatilizing between 1450° and 1600°. Sp. g. = 7.293 at 13°. It has a crystalline structure which can be made visible by moistening with hydrochloric acid, whereupon peculiar frost-like etch-figures are produced on the surface (tin-moirée). When tin is bent, a characteristic crackling sound (cry of tin) is heard, which is probably caused by the grating of the crystal faces on each other. Tin is very malleable and ductile; it can be beaten into very thin leaves (*tin-foil*) at the ordinary temperature, and at 100° it can be drawn out into wire. At a very low temperature and in contact with an alcoholic pink-salt solution (§ 201), tin passes spontaneously into another modification, *gray tin*, which has a lower specific gravity, 5.8. Above 20° this form changes back to white tin. If the latter is brought in contact with gray tin at ordinary temperatures (below $+20°$), it turns very slowly into gray tin, falling to powder, probably because of the increase in volume (this phenomenon is called the "tin-disease"). If it is not in contact with the gray modification, the transformation does not take place at all at ordinary temperatures, or at least not for centuries. Evidently there is a transition point of the two forms at 20°, and we are forced to the odd conclusion that, except on warm summer days, tin is in the metastable condition.

The reason why tin, even in contact with gray modification, passes so slowly into that form at ordinary temperatures is that the velocity of transformation is small in the neighborhood of the transition point; it is accelerated on moving away from that point. When the temperature sinks this acceleration is counteracted, however, by the retardation that all reactions undergo by a lowering of temperature. In many cases, therefore, there must be a maximum of the velocity of transformation, such as we have here at $-48°$; below that temperature the transformation again becomes slower.

Ordinary tin crystallizes in the tetragonal system. In addition to the gray modification there is also a third one, the rhombic modification. The transition point tetragonal$\rightleftarrows$rhombic is about 170°.

This point was determined in a unique way, namely, by measuring the velocity of flow of the metal under high pressure. For this purpose the solid metal was placed in a cylinder having a hole in the bottom, and the quantity of metal was measured that was forced out under constant pressure in the unit of time. In general, this quantity increases rapidly with rising temperature, but with tin it was found to diminish considerably when the temperature reached about 200°. This may be taken as a proof that the metal has another (third) modification. At 200° tin is so brittle that it can be easily pulverized.

Chemical Properties.—Tin is unaffected by the air at ordinary temperatures; if heated strongly, it burns with an intense white light to tin oxide, SnO_2. Hydrochloric acid dissolves it, forming stannous chloride and hydrogen. It is also attacked by nitric acid (§ 201). A boiling solution of caustic soda or potash converts it into a stannic acid salt (stannate) with the evolution of hydrogen:

$$Sn+2KOH+H_2O=K_2SnO_3+2H_2.$$

In the presence of weak acids (acetic acid) and alkalies it is very stable.

199. *Uses.*—On account of its permanence tin is used as a protective covering for metals which are attacked by the air and the above-named agencies. Many kitchen utensils are "tinned." Sheet iron is covered with a layer of tin, to protect it from rusting (§ 280), and is then known as *tin-plate*, or *sheet-tin*. This is done by simply dipping the sheet iron, which has been cleaned by hydrochloric or sulphuric acid, in molten tin.

Many **alloys** of tin are in use. *Solder* consists of tin and lead (in the ratio 2:1 or 1:1 or 1:2), and is harder than either of its components but more easily fusible. The alloys of copper and tin are called *bronzes;* their composition varies according to the purpose they serve. At present the bronzes usually contain a little lead and zinc as well. Bronze is hard and tough, can be easily worked and fuses to a mobile liquid, hence it is particularly suitable for casting. *Gun metal* contains 90% copper and 10% tin; *bell metal* 20–25% tin, the rest being copper. *Phosphor bronze* is prepared by fusing copper with tin phosphide (§ 202). The resulting mass is remarkably homogeneous and contains 0.25–2.5% phosphorus and 5–15% tin. Its great hardness and firmness render it especially valuable for certain parts of machines (axle-bearings). *Silicon bronze* contains silicon in place of phosphorus, is very hard and conducts electricity well, hence it is used for making telephone wire. *Tin amalgam* forms the metallic coating of mirrors.

Compounds of Tin.

Tin forms two sets of ocmpounds; they correspond to the oxygen compounds, *stannous oxide*, SnO, and *stannic oxide*, SnO_2.

STANNOUS COMPOUNDS.

200. Stannous chloride, $SnCl_2$, is prepared by dissolving tin in hydrochloric acid:

$$Sn+2HCl=2SnCl_2+H_2.$$

It crystallizes with two molecules of water, which are given off at 100°. It is very readily soluble in water (1 part in 0.37 at ordinary temperatures). Anhydrous stannous chloride is white and transparent; it melts at 250° and boils at 606°. A little above the boiling-point the vapor density corresponds to the formula Sn_2Cl_4; above 900°, however, to $SnCl_2$.

The aqueous solution acts strongly reducing. It absorbs oxygen from the air with the partial formation of basic chloride (a white powder), if the liquid is not too acidic:

$$3SnCl_2 + H_2O + O = SnCl_4 + \underset{\text{Basic chloride.}}{2Sn(OH)Cl}.$$

But if the liquid is strongly acid the tetrachloride $SnCl_4$ is also formed in this oxidation.

This same basic chloride also results from hydrolytic dissociation, when a neutral stannous chloride solution is strongly diluted.

$$SnCl_2 + aq = Sn(OH)Cl + HCl + aq.$$

The reducing power of stannous chloride is farther seen in its action on potassium permanganate, potassium dichromate, cupric chloride, mercuric chloride, etc., all of which are converted into lower stages of oxidation in acid solution.

It may be remarked here that, from the ionic point of view, oxidation amounts in many cases to raising an ion to a higher positive potential, and reduction to the reverse. Let us consider, for instance, the reaction between stannous chloride and mercuric chloride. This can be expressed by the equation

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg.$$

Stannous chloride is oxidized to stannic chloride; at the same time mercuric chloride is "reduced" to the metal. Written in ions, this equation becomes

$$Sn^{\cdot\cdot} + Hg^{\cdot\cdot} = Sn^{\cdot\cdot\cdot\cdot} + Hg;$$

that is, the electrical charge of the mercury ion is taken by the bivalent tin ion, the former losing its electrification.

Another example is the action of chlorine on stannous chloride, by which the latter is "oxidized" to stannic chloride;

$$SnCl_2 + Cl_2 = SnCl_4.$$

The ionic reaction is

$$Sn^{\cdot\cdot} + 2Cl' + Cl_2 = Sn^{\cdot\cdot\cdot\cdot} + 4Cl'.$$

Tin takes up two more positive charges, but this necessitates that the two Cl atoms become ions; they thus require two negative charges; but when these are formed two positive charges are obtained at the same time. However, the $Sn^{\cdot\cdot\cdot\cdot}$ and Cl' ions unite to form stannic chloride, $SnCl_4$, which is a very weak electrolyte (*cf.* § 201).

In the preparation of chlorine, hydrochloric acid is "oxidized" by manganese dioxide:

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2,$$

or

$$MnO_2+4H^{\cdot}+4Cl'=Mn^{\cdot\cdot}+2Cl'+2H_2O+Cl_2;$$

the positive charge of the four $H^{\cdot}$ ions is thus transferred, half to the manganese and the rest serving to discharge two chlorine ions, i.e. to equalize their negative charges.

Various *double salts* of stannous chloride are known, e.g. $SnCl_2\cdot 2KCl$; $SnCl_2\cdot 2NH_4Cl$.

Stannous hydroxide, $Sn(OH)_2$ is precipitated when a solution of stannous chloride is treated with soda:

$$SnCl_2+Na_2CO_3+H_2O=Sn(OH)_2+2NaCl+CO_2.$$

This hydroxide is insoluble in ammonia, but soluble in alkalies; when the latter solution is boiled, tin is deposited and alkali stannate, e.g. K_2SnO_3, formed. The hydroxide is also soluble in acids, thus displaying a basic as well as an acidic nature. Such compounds are able to give hydroxyl ions ($Sn^{\cdot\cdot}+2OH'$) on the one hand and hydrogen ions ($SnO_2''+2H^{\cdot}$) on the other. They are termed **amphoteric compounds.**

Stannous oxide is obtained by heating the hydroxide in a current of carbon dioxide; it is a dark-brown powder, which takes fire in the air, burning to stannic oxide, SnO_2.

Other salts of stannous oxide than the above-mentioned stannous chloride are also known. The sulphate, for instance, is obtained by dissolving the hydroxide or the metal in dilute sulphuric acid. It forms a basic salt readily.

Stannous sulphide, SnS, is precipitated as an amorphous brown powder when hydrogen sulphide is passed into the solution of stannous salts. It is insoluble in potassium sulphide, K_2S, but it dissolves to form a sulpho-stannate when brought in contact with the poly sulphide of ammonium or potassium, $K_2S_x(x=2–5)$.

$$SnS+K_2S_2=K_2SnS_3.$$

Stannous sulphide can also be prepared by fusing tin with sulphur. It then forms a bluish-gray crystalline mass.

STANNIC COMPOUNDS.

201. Stannic chloride, $SnCl_4$, was prepared as early as 1605. It was named *spiritus fumans Libavii*, after its discoverer. It is obtained by the action of chlorine on tin or stannous chloride. Stannic chloride is a liquid which fumes strongly in the air; it boils at 113.9°, and has a specific gravity of 2.234 at 15°. When brought in contact with a little water or on taking up moisture from the air, it goes over into a semi-solid, crystallized mass, $SnCl_4\cdot 3H_2O$, the so-called *tin-butter*. A fresh solution of stannic chloride is a very poor conductor of electricity. However, the conductivity increases slowly at ordinary, faster at higher, temperatures; after several days it reaches a maximum. In the case of more dilute solutions this maximum is much higher. These facts can be explained by assuming that stannic chloride is but feebly ionized and that it reacts with water in the following way:

$$SnCl_4+4H_2O \rightleftarrows Sn(OH)_4+4HCl;$$

in other words, that it undergoes hydrolytic dissociation. It is the liberated hydrochloric acid that causes the conductivity. The solution contains tin hydroxide in the colloidal state. The water has thus split up the stannic chloride into a basic hydroxide and an acid.

Stannic chloride forms well-crystallized double salts with the alkali chlorides, e.g. $SnCl_4\cdot 2KCl$ and $SnCl_4\cdot 2NH_4Cl$. The latter is known as *pink salt* (because of its color) and is used as a mordant in dyeing. Tin tetrachloride also unites with the chlorides of the metalloids to form crystallized substances, e.g. $SnCl_4\cdot PCl_5$; $SnCl_4\cdot POCl_3$; $SnCl_4\cdot SCl_4$, etc. It combines with hydrochloric acid, forming a leafy-crystalline mass, $H_2SnCl_6\cdot 6H_2O$, which melts at 9°.

Tin fluoride, SnF_4, itself is not known, but there is a compound, K_2SnF_6, which corresponds to potassium fluo-silicate; the salts of hydrofluostannic acid are isomorphous with the analogous silicon compounds.

Stannic oxide, SnO_2, can be prepared synthetically by heating tin in air. It is an amorphous white powder, insoluble in acids and alkalies; the latter, however, dissolve it when fused, forming stannates.

Stannic Acid and Metastannic Acid.—The hydroxides corresponding to SnO_2 have only very weakly basic properties; here the acidic properties are prominent. The normal hydroxide, $Sn(OH)_4$, is unknown, but there is a hydroxide of the empirical composition $H_2SnO_3(=Sn(OH)_4-H_2O)$, corresponding to carbonic acid, H_2CO_3. Strangely enough this exists in two modifications, which differ from each other both chemically and physically; they are called stannic and metastannic acids.

The **stannic acid** is precipitated when ammonia is added to an aqueous solution of stannic chloride or hydrochloric acid to a potassium stannate solution. This precipitate reacts acid when moist and is soluble in concentrated hydrochloric and nitric acids, as well as in alkalies. It gradually changes into metastannic acid.

Metastannic acid is generally prepared by treating tin with strong nitric acid; it is then formed in a vigorous reaction as a dense white powder. Metastannic acid is insoluble in sodium hydroxide, but nevertheless unites with it to form sodium metastannate; this is dissolved by water, although with difficulty, but is insoluble in the caustic soda solution. When boiled with hydrochloric acid, metastannic acid goes over into a chloride, which is insoluble in the concentrated acid but soluble in water. This solution does not contain the ordinary tin chloride, but another one, meta-tin chloride, having, however, the same composition, $SnCl_4$. It is distinguished from the ordinary stannic chloride by giving a yellow coloration with stannous chloride solution; the solution of the ordinary chloride does not do this till after some time, during which the metachloride is formed in it.

Stannic acid and the corresponding chloride thus pass over into the meta-compounds spontaneously; on the other hand, metastannic acid can be converted into the ordinary tin compounds by boiling it for some time or fusing it with a caustic alkali.

The difference between stannic and metastannic acids was pointed out by BERZELIUS as early as the beginning of the nineteenth century; nevertheless we are still without a satisfactory explanation of the matter. Inasmuch as the salts of metastannic acid, however, have in general a very complicated composition similar to the polysilicates (§ 195), it is probable that metastannic acid is a polymer of the ordinary stannic acid, i.e. that its molecule is represented by $(H_2SnO_3)_x$, stannic acid itself being H_2SnO_3.

Of the salts of stannic acid, the sodium stannate, $Na_2SnO_3 + 3H_2O$, is especially well known. It comes on the market under the name of "preparing-salt" and is used as a mordant in dyeing. It is made by fusing tin-stone with caustic soda and crystallizes in hexagonal crystals, which are more soluble in cold than in warm water.

Purple of Cassius is obtained when a mixture of the hydrosols of tin dioxide and gold is precipitated by adding some such electrolyte as ammonium chloride. This mode of formation proves that the substance is not a compound of the two components, as was formerly believed, but only a mixed gel.

202. **Stannic sulphide,** SnS_2, falls out as a yellow amorphous powder, when hydrogen sulphide is passed into the acid solution of a stannic compound. It can be synthesized by heating tin amalgam with sulphur and ammonium chloride, being thus obtained in the form of transparent golden leaves and known as *aurum musivum,* or *mosaic gold;* it is used for gilding. Stannic sulphide is a sulpho-anhydride; the corresponding sulpho-acid, H_2SnS_3, is not known in the free state, but exists in the form of salts.

Sodium sulphostannate, $Na_2SnS_3 + 2H_2O$, crystallizes in colorless octahedrons. When its solution is treated with an acid, stannic sulphide is precipitated.

Tin phosphide serves, as was stated above, for the manufacture of phosphor bronze. Of the various compounds of tin and phosphorus, the best known is the compound Sn_9P. It forms a coarsely crystalline mass, which melts at 170°.

LEAD.

203. Among the lead ores the most important is *galenite* (PbS); it occurs in isometric crystals (cubes) of a graphitic color. Other ores are *cerussite* ($PbCO_3$), *crocoite* ($PbCrO_4$), *wulfenite* ($PbMoO_4$), etc. For the extraction of the metal galenite is used almost exclusively. This is roasted to convert the sulphide partially into oxide, and partially into sulphate:

$$PbS + 3O = PbO + SO_2; \quad PbS + 2O_2 = PbSO_4.$$

In roasting care is taken that a considerable portion of the ore remains as sulphide. On farther heating, the latter reacts with the oxygen compounds in the following way:

$$2PbO + PbS = 3Pb + SO_2; \text{ and } PbSO_4 + PbS = 2Pb + 2SO_2.$$

Physical Properties.—Lead is a soft ductile metal of a bluish color. On exposure to the air it loses its lustre rapidly, becoming coated with a very thin layer of oxide. It has a specific gravity of 11.254, melts at 334°, and at white heat distils.

Chemical Properties.—The thin coating formed by the oxide on the brilliant surface of the metal protects the lead from further attack by the air. If, however, it is prepared in a very finely divided state, e.g., by heating lead tartrate or citrate in the absence of air, it takes fire in the air even at ordinary temperatures. (Other metals can be reduced in a similar way to a fine state of division, whereupon they ignite spontaneously in the air. A substance which exhibits this phenomenon is called a pyrophorus.) When lead is melted, it becomes coated with red oxide of lead; by constantly removing the latter, the lead can be entirely oxidized. A compact mass is unaffected by sulphuric or hydrochloric acid, but, when finely divided, it reacts to form the corresponding salts. Nitric acid easily dissolves it to form the nitrate. Acetic acid and various vegetable acids attack it; since all lead salts are very piosonous and very serious effects result from chronic poisoning with insignificant but successive amounts, it is not admissible to use tin containing lead in tin-plating vessels for use in the kitchen.

Zinc and iron precipitate the metal from solutions. A piece of zinc becomes covered with a dendritic crystalline mass ("lead-tree"). This reaction can be expressed by:

$$Zn + Pb^{\cdot\cdot} = Zn^{\cdot\cdot} + Pb,$$

i.e. zinc is changed into the ionic condition, and the lead ions are discharged. How it comes about that one metal thus assumes the electrical charge of another may be explained by a hypothesis of NERNST. His supposition is that every metal on coming in contact with water or a solution tends to send positive ions into it. This emission of ions continues until the positive charge acquired by the solution and the negative charge created on the metal balance by their mutual attraction the tension (called the *electrolytic solution-tension*) with which the ions are driven into the solution. This tension differs considerably for different metals; for zinc it is much greater than for lead. When, therefore, a strip of zinc is dipped in a lead solution it forces zinc ions into the solution and the zinc thus becomes much more negatively charged than would a piece of lead by the emission of lead ions. The lead ions are therefore attracted by the zinc and discharged, i.e. lead is precipitated from the solution. This process stops only when all the lead of the solution has been replaced by zinc.

Distilled water, from which the air has been entirely removed by boiling, has no effect on lead, but the simultaneous action of air and water produce lead hydroxide, which is somewhat soluble in water. This hydroxide is converted into insoluble basic carbonate by carbonic acid.

From a hygienic standpoint these properties of lead are of vast importance, because drinking-water is almost universally conducted through pipes made of lead or material containing lead ("compo-pipes"). The absorption of lead from such pipes by water and the continuation of the process depends in a large measure on the proportion of salt in the water. As a rule, the less of salts it contains, the more lead it takes up. Rain-water, which is almost entirely free from solid matter, but contains oxygen, carbon dioxide and traces of ammonia, is, therefore, most likely to dissolve lead. The lead eave-troughs, etc., which were once extensively used, should, therefore, be rejected, in case the rain-water is used for drinking. Well-water usually contains acid calcium carbonate and gypsum; as a result, the lead pipes soon become coated with an insoluble layer of lead sulphate and basic carbonate (as well as calcium carbonate), so that after a while the lead can no longer be absorbed by the water.

Lead is used for many purposes, not only in the elemental condition, but also in the form of alloys (see § 199).

Oxides of Lead.

204. The following oxides of lead are known: Pb_2O, PbO, Pb_2O_3, Pb_3O_4, PbO_2.

Lead suboxide, Pb_2O, is a velvet-black powder, which readily turns to lead oxide on heating in the air.

Lead oxide, PbO, is the only one of these oxides with basic properties. It is formed by direct synthesis from its elements (§ 203). It is fusible, and congeals again to a reddish-yellow mass called *litharge*. By carefully heating lead, lead hydroxide or lead nitrate, the oxide is obtained as an amorphous brown powder (*massicot*). It is somewhat soluble in water, forming the hydroxide. It dissolves in caustic potash, and crystallizes out in rhombic prisms on cooling.

Lead hydroxide, $Pb(OH)_2$, is formed by precipitating a lead solution with an alkali. It is soluble in caustic alkalies, but insoluble in ammonia. On being warmed to 145° it gives up water and turns to oxide. It is somewhat soluble in water, imparting to the latter an alkaline reaction, and absorbs carbon dioxide from the air.

Minium, or **red lead,** Pb_3O_4, is prepared by heating lead oxide or white lead in the air for quite a while at 300–400°. Because of its pleasing red color it is used as a pigment in painting. Gentle heating makes the color a brighter red at first; stronger heating turns it violet and finally black; on cooling, however, the original color returns. By treating it with dilute nitric acid, lead nitrate and lead peroxide are formed, hence minium may be regarded as $2PbO \cdot PbO_2$.

Lead peroxide, PbO_2, is obtained in the way just stated; more easily, however, by passing chlorine into an alkaline lead solution or adding a hypochlorite to a lead salt, thus:

$$2PbCl_2 + Ca(OCl)_2 + 2H_2O = 2PbO_2 + CaCl_2 + 4HCl.$$

Milk of lime is then added to neutralize the free acid.

Lead peroxide is an amorphous dark-brown powder. It has the property, common to most peroxides, of giving up oxygen easily. At an elevated temperature it splits up into lead oxide and oxygen. On warming it with sulphuric acid, lead sulphate and oxygen are formed; on warming with hydrochloric acid, lead chloride and chlorine are produced.

Lead peroxide, like the oxides CO_2 and SnO_2, has the character of an acid anhydride; it is soluble in hot concentrated potassium hydroxide and this solution, on cooling, deposits crystals of the composition $K_2PbO_3 + 3H_2O$ (which are thus entirely analogous in composition to potassium stannate). This *plumbate* is easily decomposed by water into potassium hydroxide and lead peroxide. If we regard lead peroxide as an acid anhydride, minium can be considered as the lead salt of the normal plumbic acid, $Pb(OH)_4$, i.e. $Pb_2 \cdot PbO_4$. This idea is confirmed by the following method of formation: If a solution of lead oxide in potassium hydroxide is added to a solution of the plumbate K_2PbO_3, a yellow substance is precipitated having the composition $Pb_3O_4 \cdot H_2O$, which gives off water readily and forms minium.

If a mixture of litharge and calcium carbonate is heated in a current of air at 700°, carbon dioxide is given off, oxygen absorbed and calcium plumbate, $CaPbO_3$, formed. If this plumbate is treated with carbon dioxide at about the same temperature, calcium carbonate and lead oxide are again formed, while oxygen escapes. This process (discovered by KASSNER) serves for the commercial manufacture of oxygen. The latter is brought on the market compressed in iron bottles (*cf.* also § 262).

The oxide Pb_2O_3 is obtained by adding sodium hypochlorite to a solution of lead oxide in potassium hydroxide. It can be regarded as the lead salt of a lead acid, H_2PbO_3, i.e. as $Pb \cdot PbO_3$, for, on treatment with dilute nitric acid PbO_2 (the anhydride of H_2PbO_3) and lead nitrate are formed.

Halogen Compounds.

205. The halogen compounds of lead having the formula PbX_2 are difficultly soluble in cold water; lead fluoride is almost insoluble and the solubility of the three others decreases with increasing atomic weight of the halogen.

Lead chloride, $PbCl_2$, is obtained as a white precipitate when dilute hydrochloric acid is added to the solution of a lead salt. At 12.5° it dissolves in 135, at 100° in less than 30, parts of water and crystallizes from the hot solution in the form of white silky needles or lamellæ. If an aqueous solution of lead chloride is treated with dilute hydrochloric acid, lead chloride is precipitated, for by the addition of Cl-ions the solubility product of lead chloride is exceeded; nevertheless, lead chloride is easily soluble in concentrated hydrochloric acid. This must be due to the formation of a compound of the chlorides of lead and hydrogen, an analogue of which has been found in $PbI_2 \cdot HI + 10H_2O$, which has been isolated. A characteristic compound of lead is the iodide PbI_2, which is precipitated from lead solutions by potassium iodide. It is scarcely soluble in cold, but moderately soluble in hot water. It crystallizes out of a solution in dilute acetic acid in beautiful crystal flakes with a golden lustre.

Lead tetrachloride, $PbCl_4$, is formed when a solution of lead dichloride in strong hydrochloric acid is saturated with chlorine. From this liquid ammonium chloride precipitates a lemon-yellow crystalline substance, $2NH_4Cl \cdot PbCl_4$, having a composition analogous to pink-salt (§ 201).

Other Lead Salts.

206. Lead nitrate, $Pb(NO_3)_2$, is obtained by dissolving lead in dilute nitric acid. It is colorless, crystallizes isometric and is soluble in 8 parts of water. Heating decomposes it (§ 122). Several basic lead nitrates are known

Lead sulphate, $PbSO_4$, is practically insoluble in water and can therefore be obtained by precipitating a lead solution with dilute sulphuric acid or a soluble sulphate. It occurs as a mineral in crystallized form under the name of *anglesite;* it is isomorphous with the sulphate of barium, barite. Lead sulphate is soluble in concentrated sulphuric acid; hence the crude acid which is concentrated in lead pans (§ 186, 3) contains lead sulphate; this is precipitated on diluting the acid with water. It is dissolved by concentrated alkalies. Ignition on charcoal reduces it to sulphide.

Lead disulphate, "plumbic sulphate," $Pb(SO_4)_2$, separates from the acid around the anode when sulphuric acid of 1.7–1.8 specific gravity is electrolyzed between lead electrodes. It has not been obtained quite free from lead sulphate. It is a white granular substance of strong oxidizing properties. Water decomposes it readily into sulphuric acid and lead peroxide. It is isomeric with **lead persulphate,** PbS_2O_8, a salt of the dibasic persulphuric acid.

Lead carbonate, $PbCO_3$, is deposited when a solution of the nitrate is treated with ammonium carbonate. *White lead,* a basic carbonate, is used extensively as a pigment. However, it soon turns black, if any hydrogen sulphide (from drainage pipes, etc.) comes in contact with it; moreover, it is injurious to the health, because it comes off of the painted walls in the form of dust and gets into the lungs. White lead is particularly valuable for its *covering-power,* i.e. the painted surface appears perfectly white when covered with only a very thin layer of the pigment; it is much greater than that of other white pigments, such as white zinc and barite, which are frequently substituted for white lead because they are harmless.

The manufacture of white lead is still carried on extensively after the Dutch method. This consists in placing rolls or "buckles" of lead-plate into jars containing a little acetic acid. The vessels are loosely covered with a leaden lid and buried in a heap of horse-manure. The heat generated by the decaying manure causes a part of the acetic acid to evaporate and converts the lead into basic lead acetate. The latter is then transformed to white lead by the carbon dioxide given off from the decaying heap. After about five or six weeks the plates are almost entirely changed to white lead. This is then ground moist, washed out (to remove any acetate) and dried whereupon it is sent to the market.

Lead sulphide, PbS, is black and comes down amorphous when hydrogen sulphide is passed into a lead solution. A liquid containing only traces of lead is colored brown by sulphuretted hydrogen; this is a very delicate means of testing for lead. Strong nitric acid oxidizes it readily to lead sulphate.

SUMMARY OF THE CARBON GROUP.

207. The elements *carbon, silicon, germanium, tin* and *lead* form a natural group, as may be seen from a comparison of their physical and chemical properties. In the following table the most important physical constants are summarized; here, as in other natural groups, the gradual change of these constants with the rise of the atomic weight is very evident:

	C.	Si.	Ge.	Sn.	Pb.
Atomic weight.	12.00	28.4	72	118.5	206.9
Specific gravity.	2.25 3.6	2.49	5.5	7.29	11.39
Melting-point.	....	very high	circa 900°	233°	334°
Boiling-point.	above 3000°	....	....	circa 1500°	circa 1600°

With respect to the chemical properties we note in the first place that all these elements have the same compound-types, MX_2 and MX_4; in other words, that they are bi- or quadri-valent; this is even true of lead (PbO_2, $PbCl_4$, etc.), which does not fit into the table of physical properties with its boiling- and melting-points. Moreover, there is to be noted in general a transition from metalloid to metallic character, as is plainly shown by the following facts:

1. Only carbon and silicon are known to form hydrogen compounds (of an indifferent nature).

2. Of the oxygen compounds of the MO type, that of carbon is indifferent and the others (no such compound of silicon is known) grow more basic in character as the atomic weight increases, lead hydroxide having rather strongly alkaline properties.

3. The oxygen compounds, RO_2, however, are decidedly acidic in character in the cases of carbon and silicon and also in the case of germanium, while in that of lead the salts of the acid H_2PbO_3 are immediately decomposed by water, so that here the acid properties appear much weakened.

4. As to the halogen compounds, those of carbon (CX_4) are unaffected by cold water—perhaps because of their insolubility in it; the other halogen compounds, MX_4, are decomposed by water.

Lead, in some of its physical and chemical properties, does not display the gradation which is ordinarily met with in the elements of a group. This phenomenon is quite often observed in elements of very high atomic weight. In the nitrogen group we saw it in the case of bismuth.

METHODS OF DETERMINING ATOMIC WEIGHTS.

208. So far only one method of determining the atomic weight has been mentioned (§ 34). This consists in investigating as large as possible a number of gaseous compounds of the element as to their vapor density and empirical composition and then calculating how many grams of the element are contained in a mole of the various compounds. The smallest figure thus found is taken as the atomic weight. Although this method is quite general, it has the drawback of affording only a certain degree of probability, a probability which becomes greater as the number of investigated compounds increases and which lessens the chance of finding a compound that contains per mole only a simple fraction of the previously accepted atomic weight.

There are, however, other methods. None of them is so generally applicable as this, but they are of a more absolute character and have been of great value in the many cases in which they could be used. They furnish a very valuable check on the determinations made by the general method. These methods are based on the following laws:

1. The **law of Dulong and Petit.** *The product of the atomic weight of a solid element and its specific heat is about* 6.4. This is evident from the table on the opposite page.

Most of the values of the product lie as the table shows, very close to 6.4; the maximum is 6.9, the minimum 5.0. Calling this product the **atomic heat,** we can express the law of Dulong and Petit in the following simple way: *The atomic heat of the solid elements is approximately constant and is about* 6.4.

A few deviations have been pointed out in the last column; in such cases it has frequently been found, however, that at an increased temperature the atomic heat approaches the value 6.4. This is probably due to the fact that at the temperature (room-temperature) at which the measurements of the specific heat of the elements have been mainly carried out, the elements are not all in the proper physical condition for comparison. It is notably the elements with atomic weights under 35 that show the greatest deviations.

It is an interesting fact that there is a certain regularity to be found in these irregularities. The latter become more marked as the valence increases.

Element	Li	Be	B	C	Na	Mg	Al	Si	P	S
Valence	1	2	3	4	1	2	3	4	3(5)	2(4,6)
Atomic heat . .	6.6	3.7	2.8	1.9	6.7	6.1	5.8	4.6	5.9	5.7

It is easy to see how the law of Dulong amd Petit can be made use of for the determination of atomic weights. Inverting, we have $\frac{6.4}{\text{Sp. H.}} = \text{At. wt.}$

Of course the result thus obtained is only approximately correct, for the product 6.4 is not strictly constant. The method is, however, reliable enough to determine what multiple of the equivalent weight (§ 23), the exact value of which can be found by analysis, is the atomic weight.

209. 2. Closely connected with the law just enunciated is that of Neumann, which has been more carefully investigated by Reg-

Element.	Sp. H.	At. Wt.	Product.	Remarks.
Hydrogen	6	1.008	6	Liquid.
Lithium	0.941	7.03	6.6	
Beryllium	0.408	9.1	3.7	Sp. H. at 257° = 0.58; prod. = 5.2.
Boron	0.254	11.0	2.8	Amorphous. Sp. H. at 400° = 0.58; prod. = 6.4.
Carbon, amorphous	0.174	12.00	2.1	
Carbon, diamond	0 143		1.7	Above 900° Sp. H. = 0.459; prod. = 5.5.
Sodium	0.293	23.05	6.7	
Magnesium	0.250	24.36	6.1	
Aluminium	0.214	27.1	5.8	
Silicon	0.165	28.4	4.6	Crystallized. Sp. H. above 200° = 0.204; prod. = 5.8.
Phosphorus	0.189	31.0	5.9	Yellow. Sp. H. of red P = 0.1698; prod. = 5.24.
Sulphur	0.178	32.06	5.7	Rhombic.
Potassium	0.166	39.15	6.5	
Calcium	0.170	40.1	6.8	
Scandium	0.153	44.1	6.7	
Chromium	0.121	52.1	6.3	
Manganese	0.122	55.0	6.7	
Iron	0.114	55.9	6.4	
Cobalt	0.107	59.0	6.3	
Nickel	0.108	58.7	6.4	
Copper	0.095	63.6	6.0	
Zinc	0.094	65.4	6.1	
Gallium	0.079	70	5.5	
Germanium	0.077	72.5	5.6	
Arsenic	0.082	75.0	6.9	Crystallized.
Selenium	0.080	79.2	6.3	Do.
Bromine	0.084	79.96	6.7	Solid.
Zirconium	0.066	90.6	6.0	
Molybdenum	0.072	96.0	6.9	
Ruthenium	0.061	101.7	6.3	
Rhodium	0.058	103.0	6.0	
Palladium	0.059	106.5	6.0	
Silver	0.057	107.93	6.1	
Cadmium	0.054	112.4	6.0	
Indium	0.057	115	6.5	
Tin	0.054	119.0	6.5	
Antimony	0.051	120.2	6.1	
Tellurium	0.047	127.6	6.0	
Iodine	0.054	126.97	6.8	
Lanthanum	0.045	138.9	6.2	
Cerium	0.045	140.25	6.3	
Tungsten	0.033	184	6.1	
Osmium	0.031	191	5.9	
Iridium	0.032	193.0	6.1	
Platinum	0.032	194.8	6.2	
Gold	0.032	197.2	6.3	
Mercury	0.032	200.0	6.4	Solid.
Thallium	0.033	204.1	6.7	
Lead	0.031	206.9	6.4	
Bismuth	0.030	208.5	6.2	
Thorium	0.027	232.5	6.2	
Uranium	0.027	238.5	6.5	

NAULT and KOPP. This law says that *in solid compounds each element has a constant atomic heat, which varies but little from that of the free element.* The molecular heat is therefore equal to the sum of the atomic heats. If the molecular heat of solid compounds is divided by the number of atoms, the quotient must be about 6.4. In reality this quotient proved to be: for bromine compounds RBr, 6.9; for RBr_2, 6.5; for iodine compounds RI, 6.7; RI_2, 6.5. The law of NEUMANN likewise holds for many elements whose specific heat in the solid state has not been susceptible of measurement, thus e.g. for chlorine compounds: for RCl compounds the quotient referred to was 6.4, for RCl_2, 6.2, for certain double chlorides, 6.1–6.2. For other elements, like oxygen, the atomic heat found from the molecular heat of the compounds is constant, but it is about 4.0 instead of about 6.4. The same is true of hydrogen, whose mean atomic heat in solid compounds is 2.3. These figures were found by determining the molecular heat of various oxygen or hydrogen compounds and subtracting from it the known atomic heats of the other elements. If the atomic heat thus obtained is divided by the atomic weight, we have the specific heat of the element in its compounds.

The way in which the law of NEUMANN can be applied to atomic weight determinations is illustrated by the following example:

The problem is to determine the atomic weight of calcium with the help of the specific heat of sulphate of lime, $CaSO_4$, which amounts to 0.1966 according to REGNAULT.

Analysis has shown that 1 kg. anhydrous calcium sulphate contains 0.294 kg. calcium, 0.235 kg. sulphur and 0.471 kg. oxygen. The atomic heat of oxygen in compounds is 4.0 (see above), and, since its atomic weight is 16, the specific heat of oxygen in its compounds is $\frac{4.0}{16}=0.25$. In the same manner it is found that the specific heat of sulphur in compounds is $\frac{5.4}{32}=0.169$.

The heat-capacity of 0.235 kg. sulphur in compounds is therefore.	$0.235 \times 0.169 = 0.0397$
The heat-capacity of 0.471 kg. oxygen in compounds is.	$0.417 \times 0.25 = 0.1177$
Total.	0.1574

This sum subtracted from the specific heat of anhydrous calcium sulphate (0.1966) gives the heat-capacity of 0.294 kg. calcium: hence the latter is

$$0.1966-0.1574=0.0392.$$

The specific heat of calcium in its compounds is therefore

$$\frac{0.0392}{0.294}=0.133.$$

The atomic heat of calcium as a metal, we may assume with great probability, is not far from 6.4. The atomic weight will therefore amount to about $\frac{6.4}{0.133}=48$.

Now the equivalent weight of calcium is known from the analysis of calcium chloride; it is 20.0, since 35.45 parts by weight of chlorine are in combination with 20 parts of calcium. The atomic weight must therefore be this number or a simple multiple of it; evidently twice the equivalent weight, or 40, is the nearest of all the multiples to the number 48, so that 40 must be taken as the atomic weight.

The value of the atomic weight calculated from NEUMANN's law therefore serves merely to decide what multiple of the equivalent weight must be taken; for this purpose the number so obtained is sufficiently accurate.

210. 3. The law of Mitscherlich. *The crystal form of compounds having analogous chemical composition is the same:* or, in other words, *compounds of analogous chemical composition are isomorphous.* The compounds KCl, KI, KBr, e.g. are analogous in composition; they all crystallize in cubes. H_2KPO_4, H_2KAsO_4, $H_2(NH_4)PO_4$ also have an analogous composition and all crystallize in the tetragonal system. The analogous compounds $KClO_4$ and $KMnO_4$ both crystallize rhombic.

If two compounds have been proved to be isomorphous, it is very probable that their composition is analogous, whereupon the atomic weight is readily found. Let us, for example, take the case of manganese, supposing its atomic weight to be unknown; now potassium permanganate is isomorphous with potassium perchlorate, which latter is known to have the formula $KClO_4$. Analysis has shown the formula of potassium permanganate to be KMn_xO_4, x being unknown, for 39 parts (by weight) of potassium (1 atom) are combined with 64 parts of oxygen (4 atoms) and 55 parts of manganese (x atoms). From its isomorphism with $KClO_4$ it follows that its formula must be $KMnO_4$ (i.e. $x=1$), hence 55 is the atomic weight of manganese.

In determining the atomic weight of zinc we could use the isomorphism of the crystallized sulphates of magnesium and zinc. The formula of the former is $MgSO_4+7H_2O$. On the basis of the analysis of zinc sulphate and the isomorphism mentioned we have the formula $ZnSO_4+7H_2O$, from which the atomic weight is obtained in the same way as above.

The law of isomorphism was discovered as early as 1819. Since at that time the law of AVOGADRO received little attention and the determination of the specific heat was in many cases impossible, the phenomena of isomorphism were the most important means of getting information regarding the value of the atomic weight. Subsequently its importance for this purpose lessened, mainly because simpler means were found, but also because it proved to be very difficult in many cases to decide whether two substances are isomorphous. Moreover it was found that certain substances of entirely different composition are isomorphous.

A very delicate test for isomorphism is the fact that a supersaturated solution can be made to crystallize, not only by an extremely small amount of the dissolved substance itself ("sowing," or "inoculation"), but by bodies that are isomorphous with it.

Experimental Determination of Equivalent Weights.

In the methods above described the question is one of determining which multiple of the equivalent weight is the atomic weight. In order to establish the atomic weights with accuracy the equivalent weights must be determined with the greatest possible precision. The solution of this problem, which is one of fundamental importance, since all the numerical relationships of chemical reactions are based on the atomic weights, has been the object of numerous investigations in the preceding century and to-day it is still only partially accomplished.

The first atomic weight table dates from DALTON in 1805. The figures given in it were scarcely more than rough approximations. BERZELIUS (1779-1848) in the first and second decades of the century determined a long series of *equivalent numbers*, after having been first obliged in most cases to work out reliable analytical methods. The atomic weights at which he arrived were in general use for many years and really differ from the more accurate ones now employed by hardly more than a fraction of a per cent. Exceedingly accurate "atomic weight determinations" were undertaken by STAS (1813-1891). The ten atomic weights determined by him, viz. those of Ag, Cl, Br, I, K, Na, Li, S, Pb, and N, are in most cases accurate to within a few units in the second decimal place. The researches called for most exhausting and persistent labors during a long period of years.

In the last decade atomic weight determinations have been carried out on a scale of much greater refinement by MORLEY, RICHARDS, GUYE and others and the accuracy of the values has been extended another decimal place, so that now not a few of the atomic weights are established with certainty to within a few units in the third decimal place.

In determining atomic weights either purely chemical or physico-chemical methods may be employed. Both have been greatly perfected in these latter investigations and they will now be described in a few paragraphs.

As for the purely chemical methods, there are four conditions which are essential to an accurate determination of an atomic weight: (*a*) A suitable substance must be found which can be prepared perfectly pure. (*b*) This compound must contain in addition to the element under study only elements of accurately known atomic weight. (*c*) The valence of the elements in this compound must be well defined. It is not permissible, for example, that the substance be a mixture of two stages of oxidation. (*d*) The compound selected must be adapted to an exact analysis, or else its exact synthesis from the weighed elements must be possible.

Notwithstanding the simplicity and legitimacy of these demands it is often difficult to satisfy them. The preparation of a compound in the pure state is among the most difficult of operations, if by purity we mean the reduction of the impurities to a 10^{-4} part of the whole. It was formerly believed that this could be readity accomplished by recrystallization, but now we know that every substance that separates out in a solid phase has a tendency to retain upon its surface or in its interior a part of the other substance contained in the phase out of which the solid separated. All precipitates or crystals from aqueous solutions contain water that is not in chemical combination. Even the splendid glistening silver crystals that are obtained in the electrolysis of a silver nitrate solution and are apparently perfectly dry and pure contain not only water but silver nitrate as well. Silver chloride, precipitated from a solution of sodium chloride by silver nitrate, may have included traces of $NaCl$, $AgNO_3$ or $NaNO_3$, even after a thorough washing. Potassium chlorate, though much less soluble than potassium chloride, contains nevertheless 0.027% of the latter after repeated recrystallizations. One of the most troublesome sources of error in all quantitative researches is the unsuspected presence of hygroscopically held water, since it is not at all easy to detect by chemical tests and causes no essential change in the external appearance of the substance containing it.

The analysis of a substance resolves itself in most cases into a separation of its components in the form of other compounds and weighings of the latter. For example, in order to determine the silver content of silver nitrate the metal is thrown down as silver chloride and the latter is weighed, whereupon the quantity of silver can be calculated from the known silver content of the chloride. The analyst generally finds it also necessary to convert one compound into another quantitatively. The modern investigations of atomic weights have also taught us that this is often a very difficult problem. Among other sources of error in this connection are the solubility of the so-called "insoluble" substances and the solubility of glass. It has long been known that substances like silver chloride, barium sulphate, etc., are not strictly insoluble; but their solubility has first received proper attention in connection with the recent atomic weight determinations. In working with glass vessels it is impossible to avoid silicic acid as an impurity. Recognition of this fact has led to the use of vessels of quartz or, better still, of platinum, which has proved to be an important refinement of method.

Physico-chemical methods have found application in the determination of the volume weight of gases. One of the most fruitful of modern physical concepts is that of the ideal gas, whose expansion at constant pressure or pressure increase at constant volume both have a coefficient for a temperature change of one degree of exactly 1/273.08. Moreover, the ideal gas is in strict accord with BOYLE's law. A gram molecule of such a gas at 6° and 760 mm. Hg pressure would occupy a volume of 22.412 l. However, the actual gases are more compressible and expansible than the ideal gas; hydrogen and helium are the only ones that are less compressible. For this reason 22.412 l. of an actual gas at 0° and 760 mm. Hg contains a little more than one gram molecule. If we let $1+\lambda$ represent the number of gram molecules of an actual gas which are contained in 22.412 l., the molecular weight of the gas becomes

$$M=\frac{22.412\,G}{1+\lambda},$$

where G is the weight of a liter of the gas under normal conditions. The establishment of the atomic weight of a gas thus resolves itself into the accurate determination of the magnitudes G and λ. The methods for ascertaining the exact weight of a given volume of a gas have undergone important improvements in recent years. The agreement of the values found by the different investigators is within ±0.0001. While formerly the gases were weighed in huge globes, some containing as much as 21 l., later investigators have been able to reduce this volume to between one liter and half a liter, or even less. Nevertheless the concordance between the various series of determinations was improved, because the corrections for the small globes were much less. An additional correction was applied for the contraction of a globe on evacuation, due to the external pressure of the atmosphere reducing the volume slightly; the buoyancy effect of the air is somewhat less for an evacuated globe than for one filled with gas.

In order to remove completely the layer of air that has been condensed on the inner surface of the globe, it is necessary to evacuate the latter repeatedly to as low a vacuum as possible and to fill it with the gas whose density is to be determined, great care being taken meanwhile to exclude the air.

Furthermore, the purification of the gases to be weighed is much better accomplished by first liquefying them and then removing the impurities by fractional distillation at a low temperature.

The determination of the quantity λ can be accomplished in four different ways, which are found described in the larger physics manuals. It should be noted, however, that they have not yet attained the exactness that characterizes the methods of determining G. In the cases of the less easily condensed gases, like H, N, O, and Cl, however, very accurate determinations have already been made.

From an experimental standpoint these physico-chemical methods have a decided superiority over the purely chemical methods in that physical measurements only are carried out after the gas has been obtained pure. All the uncertainties that are involved in chemical transformations are thus avoided; and upon such transformations every purely chemical determination of an atomic weight is based.

THE PERIODIC SYSTEM OF THE ELEMENTS.

211. In studying the elements which we have considered so far, we have found that they can be arranged into groups of elements according to their valence, the elements of each group showing great similarity in the types of their compounds. The physical and chemical properties of the elements of such a group are found to change progressively as the atomic weight increases. The question now arises whether all elements can be thus arranged into groups; the reply is affirmative.

In the course of the last century there was no lack of attempts to arrange the elements into groups of similar elements. DOEBEREINER called attention to a simple relation between the atomic weights of kindred elements as early as 1817, and in 1829 he presented the doctrine of *triads*, i.e. he showed that there are different groups of three elements each, which have a great similarity among themselves and a constant difference in the atomic weights, e.g. Cl, Br, I; Ca, Sr, Ba, etc. In the year 1865 the *law of octaves* was proposed by NEWLANDS, he having discovered that, if the elements are arranged according to increasing atomic weight, after an interval of seven elements an element follows which has properties analogous to those of the first, i.e. the first, eighth, fifteenth, etc., are similar. In 1869 MENDELÉEFF and LOTHAR MEYER almost simultaneously reached conclusions which are comprehended by the term "periodic system."

If we arrange the elements according to increasing atomic weight, thus:

						H 1
Li 7	Be 9.1	B 11	C 12	N 14	O 16	F 19
Na 23	Mg 24	Al 27.1	Si 28.4	P 31.0	S 32	Cl 35.4

we see that there is a *gradual* variation in the properties of elements in a horizontal line; after fluorine, however, a small increase in the atomic weight involves a *sudden* change of properties. Moreover those elements which are in the same vertical column show great similarity, as we saw above in the cases of carbon and silicon, nitrogen and phosphorus, etc.

This regular change makes itself evident in the valence toward oxygen, which rises from *one* (with Li and Na) to *two* (Be, Mg), *three* (B, Al), *four* (C, Si), *five* (N, P), *six* (S) and *seven* (Cl in Cl_2O_7). The valence toward hydrogen or a halogen increases, however, from *one* (Li) to *four* (C) and then falls again to *one* (F). A similar regular change is to be observed with reference to the physical properties, e.g. specific gravity and atomic volume.

	Na	Mg	Al	Si	P (red)	S	Cl (liq.)
Sp. gravity............	0.97	1.75	2.67	2.49	2.14	2.06	1.33
At. volume...........	24	14	10	11	14	16	27

By *atomic volume* we understand the atomic weight divided by the weight of the unit volume (based on water of 4° as 1); it is therefore the number of cubic centimeters occupied by a gram-atom.

Here we observe an increase of the specific gravity up to aluminium, then again a decrease to chlorine, while the atomic volume, on the other hand, decreases from the beginning of the series to aluminium and then increases. This steady change of the same physical properties is also observed in the compounds of the above elements. For the oxides, e.g. we have:

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Sp. gravity.............	2.8	3.7	4.0	2.6	2.7	1.9	?
At. volume.............	22	22	25	45	55	82	?

Moreover, if we write down a series of elements according to increasing atomic weight, beginning with another univalent metal, we discover irregularities of exactly the same sort as the above. The following series may serve as an example of this:

	Ag	Cd	In	Sn	Sb	Te	I
Atomic wt.......	107.8	112.4	115	119.0	120.2	127.6	127.0
Sp. gravity......	10.5	8.6	7.4	7.2	6.7	6.2	4.9

Here also we find the same gradual rise of valence from silver, which is univalent, to septivalent iodine, the progressive transition from metal to metalloid and a continuous decrease in specific gravity. But more; if we put this last row under the first two:

						H 1
Li 7	Be 9.1	B 11	C 12	N 14	O 16	F 19
Na 23.1	Mg 24.4	Al 27.1	Si 28.4	P 31.0	S 32.1	Cl 35.5
Ag 107.9	Cd 112.4	In 115	Sn 119.0	Sb 120.2	Te 127.6	I 127.0,

it is apparent that the elements in the same vertical columns belong to a group. This has been demonstrated for the last four columns in preceding chapters; it will be proved for the others later on.

In the light of these facts, we are led to the conclusion that *the physical and chemical properties of the elements are functions of their atomic weights;* and when we consider the series beginning with lithium and sodium, and note that in each instance, after a difference of about 16, there follows another element with corresponding properties, we are led to the supposition that these properties are *periodic* functions of the atomic weights.

By a function we understand in general a dependent relation between two or more magnitudes, of such a sort that, when one changes, the other does likewise. In the equations $y=a\pm x$; $y=ax$; $y=x^n$, etc., y is a function of x. A **periodic** function requires that the same value appear for one magnitude in regular intervals as the other magnitude steadily increases. An example of this kind is presented by the goniometric functions, as $y=\sin x$, etc., for every time x increases by 2π, y comes to have the same value again.

If we desire to substantiate the conclusion just stated, we shall have to investigate first the length of each period, in other words, determine how many elements intervene in the table, according to increasing atomic weight between two with analogous properties.

It has already been shown that for the elements as far as chlorine, a period always includes seven elements. After chlorine comes potassium (39), which thus falls into the column under sodium. The following elements,

K 39.2 Ca 40.1 Sc 44.1 Ti 48.1 V 51.2 Cr 52.1 Mn 55.0,

correspond very well with the preceding series,

Na 23.1 Mg 24.4 Al 27.1 Si 28.4 P 31.0 S 32.1 Cl 35.5

at least so far as the valence and the form of the compound are concerned (Al_2O_3 and Sc_2O_3, TiO_2 and SiO_2, K_2CrO_4 and K_2SO_4, $KMnO_4$ and $KClO_4$), although the similarity of these elements in other respects is not very marked.

The elements following manganese, viz., Fe 55.9, Co 59.0, Ni 58.7, however, do not fit in at all under K, Ca, Sc; but if we pass these by there follows another series of seven elements, which corresponds to the one beginning with potassium:

Cu 63.6 Zn 65.4 Ga 70 Ge 72.5 As 75.0 Se 79.2 Br 80.0.

We therefore reach the conclusion that, after the first two periods of seven elements ending with chlorine must come one of seventeen elements (two of seven each, and three elements placed at the side), if the elements in the same vertical column are to correspond in their properties.

This *large period* of seventeen elements can, therefore, be arranged under the preceding *small period* of seven elements in the following way:

SMALL PERIOD.

Na23.1 Mg24.4 Al27.1 Si28.4 P31.0 S32.1 Cl35.5

LARGE PERIOD.

K39.2 Ca40.1 Sc44.1 Ti48.1 V51.2 Cr52.1 Mn55.0 Fe55.9 Co59.0
Ni58.7 Cu63.6 Zn65.4 Ga70 Ga72.5 As75.0 Se79 2 Br80.0.

In order to arrange in periods the elements whose atomic weights exceed eighty, it is again necessary to assume large periods, and, moreover, to leave several places vacant. In this manner we arrive at the scheme known as MENDELÉEFF's table (see p. 301).

As to the position of hydrogen in this table opinions are divided. MENDELÉEFF placed this element in the first group, above lithium; its chemical properties indicate without doubt that it belongs with these metals. On the other hand, ORME MASSON has presented arguments for placing it at the head of group VII, as is done in this table. These arguments are as follows:

(1 The molecule of hydrogen contains two atoms, as does a halogen molecule, while the molecule of an alkali metal consists of one atom. (2) The very low boiling-point of hydrogen indicates a similarity to the halogens; moreover the boiling-points of the alkali metals fall with

increasing atomic weight. (3) The difference between the atomic weights of the elements of a horizontal series is, on the average, 3. By placing hydrogen in group VII it differs by 3 from the next element, helium; but it is then also in good agreement with fluorine, for the mean difference in atomic weight between the successive elements of a column is 16. The difference F − H = 18, while Li − H = 6, i.e., there is no analogy in the latter case. (4) Liquid and solid hydrogen have no metallic properties. (5) The most important argument for placing hydrogen in the first group is based on its relation to the acids, which may be regarded as salts of hydrogen. But in organic compounds chlorine can replace hydrogen without essentially altering the nature of the substance. This "organic" argument thus offsets the "inorganic" one, based on the analogy of acids and salts.

As to the elements discovered in the atmosphere since 1894, viz., *helium* (at. wt. 4), *neon* (20), *argon* (40), *krypton* (81.6) and *xenon* (128), it is clear that they form a natural group, for their properties display great analogy (see § 110). Since they are not able to form compounds with other elements, they can be regarded as nullivalent. In that case their group could find a place after the eighth, or before the first, group (compare the table, page 294), thus forming a bridge, or transition, from the strongest electro-negative, to the strongest electro-positive, elements. However, it must be noted that argon with an atomic weight of 40 precedes potassium with an atomic weight of 39. As may be seen from Plate I, their atomic volumes fit into LOTHAR MEYER's curve very well.

212. Group VIII, as has been said, owes its origin to the setting at the side of the elements included in it, for by this means the corresponding elements of groups I–VII could be brought under each other. It will thus be of importance to the system, if the nine elements of this group display so much analogy to each other that the grouping of them together appears actually justified. Now this is really the case, as is seen from the following study of their properties:

1. All these elements are of a gray color and difficultly fusible; indeed, osmium is one of the hardest of all metals to fuse (2500°); iridium melts at 1950°, wrought iron at 1500°, etc. The melting-point of iron is higher than that of cobalt, and the latter higher than that of nickel. A similar fall of this constant is found with ruthenium, rhodium and palladium, and also with osmium, iridium and platinum.

2. Their atomic volumes are small in comparison with those

MENDELÉEFF'S TABLE WITH THE ATOMIC WEIGHTS IN ROUND NUMBERS.

Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.			0
Type of the Compounds: With hydrogen or a halogen; With oxygen (highest stage).	MX M_2O	MX_2 MO	MX_3 M_2O_3	MX_4 MO_2	MX_3 M_2O_5	MX_2 MO_3	MX M_2O_7	MO_3	MO_2	MO	
First period Row 1							H 1.01				He 4
2	Li 7.0	Be 9.1	B 11.0	C 12 0	N 14.0	O 16	F 19				Ne 20
Second " " 3	Na 23.1	Mg 24.4	Al 27.1	Si 28.4	P 31.0	S 32.1	Cl 35.5				Ar 39.9
Third " " 4	K 39.2	Ca 40.1	Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55.0	Fe 55.9	Co 59.0	Ni 58.7	—
" 5	Cu 63.6	Zn 65.4	Ga 70	Ge 72.5	As 75.0	Se 79.2	Br 80.0				Kr 81.8
Fourth " " 6	Rb 85.5	Sr 87.6	Yt 89.0	Zr 90.6	Nb 94	Mo 96.0	— 100	Ru 101.7	Rh 103.0	Pd 106.5	—
" 7	Ag 107.9	Cd 112.4	In 115	Sn 119.0	Sb 120.2	Te 127.6	I 127.0				X 128
" 8	Cs 132.9	Ba 137.4	La 138 9	Ce 140.3	(Di 142)?	—	Sa 150.3	—	—	—	
9	—	—	—	Er 166	–	—	—				
10	—	—	Yb 173.0	—	Ta 183	W 184	—	Os 191	Ir 193.0	Pt 194.8	
11	Au 197.2	Hg 200.0	Tl 204.1	Pb 206.9	Bi 208.5	—	—				
" 12	—	-	—	Th 232.5	—	Ur 238.5	—				

of the neighboring elements. The atomic volume of molybdenum is 11.2, that of ruthenium, rhodium and palladium about 9; that of silver 10.3; that of cadmium 13.0.

3. They display in a marked degree the ability to let hydrogen pass through at red-heat, or to condense it on themselves at ordinary temperatures. The former property is especially developed in iron and platinum, the latter in palladium.

4. It is only with these metals that we find RO_4 compounds, in other words, they are the only ones which can be octivalent. The compounds OsO_4 and RuO_4, for example, are known, and also those with carbon monoxide, as $Ni(CO)_4$ and $Fe(CO)_4$. We find here a general tendency to form compounds with carbon monoxide, e.g. $PtCl_2 \cdot 3CO$. In this last compound platinum can also be considered octivalent.

5. They form stable and, in most cases, well-crystallizing double salts with potassium cyanide. Iron, ruthenium, and osmium give compounds of the type $K_4R(CN)_6$; cobalt, rhodium, and iridium form $K_3R(CN)_6$, while the elements of the last column, nickel, palladium, and platinum, give $K_2R(CN)_4$ double salts.

6. They all form colored salts: those of cobalt are red or blue; the nickel salts are green; all the rest are of various shades of brown.

7. They all possess the ability to condense on themselves other gases than hydrogen in larger or smaller amounts; especially is this true of the platinum metals. Platinum and palladium absorb carbon monoxide greedily.

213. Let us now examine the seven other groups (vertical columns) more closely. If we bear in mind what was stated with reference to the large periods, it is apparent that not all the elements in such a group display perfect chemical analogy. Such analogy is found, however, when we compare with each other only those elements that belong to the even or the odd rows of the large periods. The similarity of the elements of these divisions is seen, in the case of the large periods, from the following facts:

1. Only the elements of the odd rows give hydrogen or alkyl compounds.

2. In the even rows the basic properties of the hydroxides are prominent, in the odd rows the acidic properties.

In general it may be said that, passing from left to right in the table, we meet first those that form the strongest bases and then gradually those that give acids. The latter property is most marked in the halogens, since they even form strong acids on combination with hydrogen.

A similar change is observed in going from the top to the bottom of the system. As the atomic weight increases, the metallic (base-forming) nature of the elements in each group becomes more predominant.

214. The periodic system of the elements is of value in four different respects:

1. In constructing a system of the elements.
2. In ascertaining the atomic weights of elements whose equivalent weights only could be determined.
3. In foretelling the properties of elements as yet undiscovered.
4. In confirming or correcting atomic weights.

Let us look at these various applications in some detail:

The Use of the Periodic Law in Constructing a System of the Elements.

215. After a careful comparison of the elements MENDELÉEFF reached the following important conclusion: *The entire character of an element, as displayed in its physical as well as in its chemical properties, is determined by the position which it occupies in the system and particularly by the four adjacent elements, the atomic analogues.* If an element is in an even series, the elements in the adjoining even series are its atomic analogues; the same is true of the odd rows. From this it follows that, when the properties of an element are exactly known, its place in the system can be assigned. A couple of illustrations will make this clear.

The element beryllium possesses marked analogy to aluminium on the one hand and magnesium on the other; therefore it was a much discussed question whether its oxide should be given the formula BeO or Be_2O_3. Since, according to analysis, 9.1 parts Be combine with 16 parts O, the atomic weight would be in the former case 9.1, in the latter $\frac{3}{2} \times 9.1 = 13.7$ With the atomic weight 13.7 the element would stand between nitrogen and oxygen; as nitrogen and the elements of the sulphur group as well yield only acid-forming oxides, beryllium oxide would have to be an acid anhydride too, which is not the case, it being a basic oxide.

Thus beryllium would not fit in the system with that atomic weight. If, however, it has the atomic weight 9.4, it falls in the horizontal series between the strongly basic lithium and the weakly acidic boron and over magnesium, with which it shows real analogy. This is indeed its fit place, i.e. its properties are those which must belong to an element in this position (see table). Farther, the properties of beryllium are to those of lithium as the properties of boron are to those of beryllium, or, in the form of a proportion: Be:Li::B:Be. Just as lithium forms a more strongly basic oxide than beryllium, so the basic character of beryllium oxide is stronger than that of boron oxide; again, beryllium chloride is more volatile than lithium chloride, boron chloride more volatile than beryllium chloride.

We also have the relation Be:Mg::Li:Na::B:Al, for beryllium oxide is less basic than magnesium oxide, lithium oxide than sodium oxide, boron oxide than aluminium oxide. Beryllium fluoride dissolves in water, magnesium fluoride does not; similarly boron fluoride, but not aluminium fluoride, is soluble in water.

Finally we have Be:Al::Li:Mg::B:Si. The hydroxides of beryllium and aluminium are very similar to each other; they are gelatinous and soluble in alkalies. Both metals are scarcely acted upon by nitric acid and both dissolve in alkalies with the evolution of hydrogen. Their chlorides must be prepared in the same way from the oxides (by heating with charcoal in a current of chlorine). Likewise lithium and magnesium are analogous in certain respects; the carbonate and the phosphate of lithium, like the corresponding salts of magnesium, are very difficultly soluble, which is in marked contrast with the other metals of the lithium group. Boron and silicon both form very refractory oxides and salts; their fluorine compounds are decomposed by water in a similar manner, etc.

The evidence in accordance with which beryllium was assigned its present position in the system was subsequently confirmed directly by the determination of the vapor density of the chloride, which led to the formula $BeCl_2$. The vapor density of the beryllium compound of an organic substance (acetylacetone) also led to 9.1 as the atomic weight of beryllium.

As a second example let us take thallium. This element displays analogy with the alkali metals and also with aluminium, as well as with lead and mercury. According to its atomic weight it must lie between the two latter and belongs in the aluminium group. This position is justified when the following relation is taken into consideration:

Tl:Al::Hg:Mg::Pb:Si.

The highest stages of oxidation show unmistakable analogy, since the oxides have the same properties by pairs. The oxides of aluminium and thallium are weakly basic, those of mercury (ic) and magnesium more strongly basic, while lead dioxide and silica are slightly acidic. Thallium, mercury and lead all form lower oxides of strongly basic character (Tl_2O, Hg_2O, PbO,) which aluminium, magnesium and silicon are unable to do. The oxide Tl_2O is comparable with K_2O in its properties, the lead monoxide with calcium oxide (Tl:K::Pb:Ca); see the table. In regard to the physical properties, it should be observed that in the matter of volatility thallium lies between mercury and lead

Use of the System in Ascertaining the Atomic Weights of Elements whose Equivalent Weights only are known.

216. A good instance is that of the very rare element indium. When the periodic system was established only the equivalent weight of indium was known, the analysis of the chloride having shown it to be 38.3, i.e. it was known that 38.3 parts of indium combine with 35.5 parts of chlorine. If this were the atomic weight and consequently In_2O the formula of the oxide, the element would have to occupy the place which potassium now has. Not only is this place taken, but the oxide is only weakly basic, while it should have strongly basic properties if it belonged to the first group. If the atomic weight were 76.6, corresponding to the oxide InO, the element would stand between arsenic and selenium in the table; its oxide could not then have the formula InO, but would have to be In_2O_5 or In_2O_3 and have acid properties. On the other hand, there is no place for a metal with the atomic weight 76.6 and an oxide InO in the second group, where the oxides have this type. If the oxide be In_2O_3, the atomic weight of indium must be 115. Now, as a matter of fact, there is a vacant place in the system between Cd = 112 and Sn = 119 for an element with an R_2O_3 oxide. In the same way as we have shown it for the oxides R_2O and RO, it can also be demonstrated that indium could not be located in the table with an oxide InO_2, In_2O_5, InO_3, etc. There remains, thus, no other possibility than to give the oxide the formula In_2O_3 and the element an atomic weight of 115.

Let us now see whether the properties of the element and its compounds conform to this location. Two of its atomic analogues for this position are cadmium and tin. The oxides of both are easily reduced; this is true also of indium oxide. If, now, we consider the metals:

Ag, Cd, In, Sn, Sb (7th series),

we notice first that the melting-point of silver lies higher than that of cadmium; likewise antimony melts higher than tin:

$$Ag > Cd; \quad Sn < Sb.$$

If indium fits in this series, it must, therefore, have the lowest melting-point of these five metals. This is actually the case; its melting-point is 176°. In the color of the metals there is a further analogy; silver, cadmium and tin are white, and so is indium. As to the specific gravity, cadmium has the specific gravity 8.6, silver 10.5; the difference is thus 1.9. The difference of the specific gravities of tin and antimony is, on the contrary, small, $7.3 - 6.7 = 0.6$. If indium stands between these two pairs of elements its specific gravity should be smaller than the mean between cadmium and tin, i.e. $\frac{1}{2}(8.6 + 7.3) = 7.9$. In reality its specific gravity is 7.42.

The position of the metal requires that its oxide be feebly basic, weaker even than the oxides of cadmium and thallium (Tl_2O_3), since cadmium is at the left and thallium farther down in the system (§ 215); on the other hand, it must be more strongly basic than the oxides of aluminium and tin. This condition also is fulfilled, as the following sets forth: the oxides of aluminium and tin, because of their slightly acid nature, dissolve in alkalies, forming definite compounds with the latter. The oxides of cadmium and thallium, however, are insoluble in alkalies; they are distinctly basic. Indium sesquioxide is soluble in alkalies, but forms no definite compound with them.

Finally, there is also the conduct of indium salts toward hydrogen sulphide which supports the placing of the element between cadmium and tin, for indium also is precipitated by hydrogen sulphide from acid solutions.

Prediction of the Properties of Elements yet Undiscovered.

217. When Mendeléeff constructed his table, the elements gallium and germanium (fifth series) were still unknown. From the properties of the atomic analogues he ventured however at that time to predict the properties of these elements; thirteen years later Winkler discovered an element with the atomic weight 72 (Mendeléeff had termed such an one "ekasilicon"; the discoverer named it *germanium*). Indeed there proved to be a very close agreement between the actual properties and those predicted, as the following summary evidences:

Properties of ekasilicon predicted by Mendeléeff.	Properties of germanium discovered by Winkler.
1. The atomic weight must be the mean of the four atomic analogues Si, Sn, Zn, Se, i.e. $\frac{1}{4}(28.4+118.5+65.4+79.1)=72.85$.	1. At. wt. $=72.5$.
2. The specific gravity (deduced as for indium above) must be 5.5.	2. Sp. g. $=5.469$ at 20°.
3. The atomic volume must lie between those of silicon (13) and tin (16), but be only a trifle above 13.	3. At. vol. $=13.3$.
4. Since it belongs in an odd series, it must be able to form alkyl compounds. Judging from analogies, the boiling-point of $Es(C_2H_5)_4$ must be 160°, its specific gravity 0.93.	4. Alkyl compounds were obtained. $Ge(C_2H_5)_4$ boils at 160° and its specific gravity is a little less than 1.
5. The acid properties of EsO_2 must be stronger than those of SnO_2.	5. GeO_2 lacks entirely the basic properties which are found to a limited extent in SnO_2.
6. The specific gravity of EsO_2 is 4.7.	6. The specific gravity of GeO_2 is 4.703 at 18°.
7. Since the oxides of indium and arsenic are easily reduced, this must also be true of EsO_2.	7. GeO_2 is easily reduced to the metal by heating with carbon or in hydrogen.
8. EsS_2, because of its analogy with SnS_2, will probably be soluble in NH_4SH.	8. GeS_2 dissolves readily in NH_4SH
9. $EsCl_4$ is liquid, boils below 100° (since the boiling-point of $SiCl_4$ is 57° and that of $SnCl_4$ 115°), and has a specific gravity of 1.9.	9. $GeCl_6$ is liquid, boils at 86°, and has a specific gravity of 1.887.
10. K_2SnF_6 being more readily soluble in water than K_2SiF_6, the solubility of K_2EsF_6 must also be greater than that of K_2SiF_6.	10. K_2SiF_6 is almost insoluble; K_2GeF_6 dissolves in 34 parts of boiling water.

Use of the Periodic System in Correcting Atomic Weights.

218. In the group of the platinum metals the atomic weights were previously determined by BERZELIUS and FREMY to be as follows: Os = 199, Pt 198, Ir 197. In this order the metals named do not, however, fit into the system, for osmium should be the first of the three on account of its analogy with iron and ruthenium, i.e. it should have the smallest atomic weight of the three. On the other hand, platinum, which is more akin to palladium, ought to have the highest atomic weight. A painstaking investigation by SEUBERT showed that in reality osmium has the atomic weight 191, iridium 193.0, and platinum 194.8, which order is in harmony with the system.

219. Graphic representation.—The fact that an arrangement of the elements according to increasing atomic weight also makes the gradual change of the physical properties apparent can be seen most clearly from a graphic representation (as proposed by LOTHAR MEYER), in which the atomic weights are the abscissas and the atomic volumes the ordinates (see Plate I at end of book).

The first thing we notice in the curve is the regular rise and fall of atomic volumes. At the beginning of each period the atomic volume is at a maximum; it reaches a minimum half way through the period (in the large periods at group VIII) and then increases again. In the descending portions are the ductile, on the ascending the brittle, elements. On the ascending portions and at the maxima are, further, the gaseous and the easily fusible elements; on the descending and at the minima the difficultly and very difficultly fusible. On the descending portions are the electro-positive, on the ascending the electro-negative, elements. The periodicity of the elements thus becomes very evident.

220. The discovery of the periodic system once more thrust into the foreground of interest one of the oldest of questions, viz., that concerning the *unity of matter*.

The striking connection between all the properties of the elements and their atomic weights leads unavoidably to the assumption of a *primordial* or *ground substance*. As to the nature of this substance no evidence is at present obtainable. PROUT, in 1815, regarded hydrogen as such a substance. He observed that the (then accepted) atomic weights of many elements, based on hydrogen as unity, are whole numbers. Later, very accurate atomic weight determinations, particularly those of STAS, which were undertaken with the purpose of testing this hypothesis, demonstrated with certainty, however, that it was untenable. *Cf.* § 267.

221. The periodic system of the elements is one of the most important discoveries in the field of inorganic chemistry; it can never lose its importance, though it is gradually becoming more evident that the system in its present form represents the relations of the elements to each other merely in an approximate way and is only a crude first attempt at a real system.

There are indeed serious objections to the periodic system, which are of such a nature that some people rather hastily declare it to be absolutely worthless. These objections concern, in the first place, the positions which certain elements occupy in the system, and which agree very poorly with their properties. This is the case, e.g., with gold and copper, which, indeed, show some analogy with lithium and sodium in their *ous*-compounds, but otherwise differ decidedly from the latter elements. The same is true of the metals of the cerium group (Ce, La, Nd, Pr, etc.). The analogy with the other elements of the same group is feeble. If the reply be made that these elements are still too little known because of their rarity and the great expenditure of energy and pains required for their investigation, it must be protested that the same is also true of those better known, such as cerium, and that if these elements should disclose themselves as complexes of several (which is not improbable), it is very doubtful whether there would be a place in the system for elements with approximately those properties which we are at present acquainted with in lanthanum. neodymium, and praseodymium, unless more than one element were put in a place, as has been proposed.

A second objection concerns the inability to fit all elements into the system. This is particularly the case with tellurium. Its physical and chemical properties put it without doubt in the sulphur group, and here there is a space for it, if its atomic weight were only about 125, or at least smaller than that of iodine (126.85). Nevertheless repeated and careful investigations have fixed its atomic weight at 127.6. The same difficulty presents itself with cobalt and nickel. According to their atomic weights the four elements Fe, Co, Ni, Cu must be arranged as follows: Fe, 55.9, Ni 58.7, Co 59.0, Cu 63.6. But the order which best corresponds with their properties is the one given first, cobalt belonging more strictly with iron, nickel with copper.

LITHIUM AND SODIUM.

Lithium.

222. This metal is not found free in nature; in combination, however, it is very widely distributed, although always in small amounts. Many mineral waters contain it. It occurs chiefly in the silicate *lepidolite*, or *lithia-mica*, also as the phosphate in *triphylite* and in company with aluminium, sodium, and fluorine in *amblygonite*. Finally, lithium is met with in the ashes of certain plants, such as tobacco, indicating that it is also contained in the soil. With the aid of the spectroscope it can be detected in very many minerals.

Lithium can be obtained from lepidolite by the following very simple process: The mineral is fused and then poured into cold water, whereupon it becomes very brittle and its silicates are brought into such a condition that they can be decomposed by hydrochloric acid. The finely powdered mass is boiled with hydrochloric acid and the metals Ca, Al, Mg, etc., precipitated by soda from the resulting solution (after filtering off the silica), lithium and the other alkali metals remaining in solution. By evaporation a salt mixture is obtained from which the lithium chloride can be isolated by extraction with alcohol, the insoluble chlorides of sodium and potassium remaining behind.

Metallic lithium is prepared by electrolysis of the fused chloride or a concentrated solution of this salt in pyridine. Next to solid hydrogen, it is the lightest of all solid substances, its specific gravity being only 0.59, so that it floats on coal-oil. It is silvery-white, but tarnishes very rapidly in moist air. Melting-point 180°. When heated in the air it burns with an intense white light to the oxide; at ordinary temperatures it is not so readily oxidized as sodium and potassium. It decomposes water with the evolution of hydrogen: the heat generated is sufficient, however, to melt the metal.

Lithium oxide, Li_2O, and **hydroxide**, $LiOH$. The former is obtained by heating the nitrate strongly. It dissolves in water slowly, forming the hydroxide. The latter is a white, crystalline substance, similar to caustic soda; it dissolves in water, producing a strongly alkaline solution.

Lithium chloride, $LiCl$, crystallizes anhydrous in regular octahedra; below 0° it takes up two molecules of water of crystallization however. It dissolves very easily in water and deliquesces in moist air.

Lithium carbonate, Li_2CO_3, unlike the carbonates of the other alkalies, is difficultly soluble in water (100 parts of water at 13° take up 0.769 part); hence it can be precipitated from the concentrated solution of the chloride by ammonium carbonate.

Lithium phosphate, Li_3PO_4, is likewise very sparingly soluble in water (1 part in 2539 parts of water), although the phosphates of the other alkalies are freely soluble. The formation of this salt serves as a test for lithium.

The *lithium spectrum* consists of two red bands, one of which in particular is easy to recognize.

Sodium.

223. Sodium occurs in nature in enormous quantities and is very widely diffused. It is a constituent of countless silicates and, as a result of rock decay, gets into the soil, whence it enters the plants and finally reaches the animal organism. The nitrate is known as *Chili saltpetre,* the chloride as *rock-salt* or *halite,* the carbonate as *soda;* the *cryolite* (ice-stone) of Greenland is a sodium aluminium fluoride. Common salt, NaCl, constitutes the main part of the saline matter in sea-water. Certain bodies of water such as the Dead Sea of Palestine, and the Great Salt Lake in North America, are almost saturated solutions of common salt.

The metal was first obtained by DAVY in 1807 by the electrolysis of molten sodium hydroxide. GAY-LUSSAC and THÉNARD got it by heating sodium hydroxide with powdered iron to white heat. The first named method is the one now generally employed for its commercial manufacture, inasmuch as electric power can be obtained quite cheaply.

For this purpose sodium hydroxide is heated a little above its melting-point. The sodium formed at the cathode is kept away from the anode by an iron net. At the anode hydroxyl groups are liberated, which yield water and oxygen. The latter escapes but the water dissolves in the molten mass and comes in contact with the sodium at the cathode, causing half of it to be changed back to sodium hydroxide, while hydrogen is evolved. As a result the maximum yield of metal for a given quantity of electricity is only 50%. If the temperature gets too high during the electrolysis, sodium dissolves in the molten mass and is oxidized at the anode.

Sodium is silvery-white, melts at 95.6° and boils at 900°, turning at the latter temperature to a colorless vapor. At ordinary temperatures it is very soft, so that it can be readily cut with a knife. It can also be easily pressed through a small hole, coming out in the form of wire. Sp. g. at 13.5° = 0.9735.

The molecule of sodium contains only one atom, as is proved by the depression of the freezing-point of its solution in tin. A great many metals have this same property.

In the moist air the bright surface of a freshly cut piece tarnishes rapidly, but in air that has been dried with phosphorus pentoxide it keeps its metallic lustre for days. Sodium can be heated in the air to melting and even still higher without catching fire. It ignites only when heated strongly, whereupon it burns with a very bright yellow light (especially in an atmosphere of oxygen). With water it generates hydrogen, sodium hydroxide being also formed. If it is held firmly in one place during this process (e.g. by laying it on a piece of filter-paper floating on water, or upon ice), the hydrogen takes fire because of the localization of the heat production.

Sodium finds extensive use in the laboratory and in the arts. Because of its strong reducing-power it is often used to obtain the elements from their oxides; magnesium and aluminium were formerly obtained thus. In organic chemistry it is also frequently employed for various purposes.

OXIDES AND HYDROXIDES OF SODIUM.

224. On burning sodium in dry oxygen a mixture of two oxides, Na_2O and Na_2O_2, results. The former is also obtained by heating sodium with caustic soda:

$$NaOH+Na=Na_2O+H.$$

The product is a gray mass, which dissolves in water, forming sodium hydroxide, $NaOH$, and giving off much heat.

The **peroxide,** Na_2O_2, is obtained by heating sodium in a current of oxygen till no more oxygen is absorbed. With 8 mols. water it forms a hydrate, $Na_2O_2+8H_2O$. Since it yields hydrogen peroxide with dilute acids and is a vigorous oxidizing-agent it is manufactured commercially.

Sodium hydroxide, $NaOH$, *caustic soda,* is formed, together with metallic sodium, when sodium monoxide is reduced in a current of hydrogen. The ordinary method of preparing caustic soda consists in boiling soda with slaked lime:

$$Na_2CO_3+Ca(OH)_2=2NaOH+CaCO_3;$$

or $$2Na^{\cdot}+CO_3''+Ca^{\cdot\cdot}+2OH'=2(Na^{\cdot}+OH')+CaCO_3.$$

As the solubility product (§ 73) of $CaCO_3$ molecules is very small, the ions $Ca^{\cdot\cdot}$ and CO_3'' must unite and the carbonate of lime sinks to the bottom. In order to make the decomposition of sodium carbonate complete, a slight excess of slaked lime is added. Nevertheless, the solution does not contain an appreciable quantity of calcium hydroxide. The reason of this is clear: In the solution there are a large number of OH-ions; as a result the number of Ca-ions can only be very small, for the value of the solubility product of calcium hydroxide is reached with even a very low concentration of the latter ions. The hydroxide is obtained by evaporation, whereupon it is generally cast into sticks for the market. It is radiate-crystalline and very hygroscopic. It dissolves in water with the evolution of considerable heat. Sodium hydroxide is a very strong base; it is used in the arts for numerous purposes, among others the manufacture of soap.

SALTS OF SODIUM.

225. The sodium salts are of great industrial importance; many of them are prepared in enormous quantities. The starting-point for their manufacture is usually common salt.

Sodium chloride, NaCl, *common salt,* is found in large masses as *rock-salt,* e.g. at Stassfurt and Reichenhall and in Galicia, where it is dug out by miners. Farther, large, amounts are obtained from sea water and the water of salt wells. Three methods are employed to remove salt. In sufficiently warm countries (e.g. Mediterranean coast, central New York State) the brine is led into flat basins of very large surface area ("salterns," or "salt covers"). In these the water is removed by solar evaporation and the salt crystallizes out. Any gypsum that may be present separates out first, whereupon the brine passes to further basins and yields pure salt. Later on, the other salts separate out; these are sometimes worked up commercially. In countries with a cold climate (e.g. on the shores of the White Sea) the water is allowed to freeze in flat basins. The ice that forms is free from salt so that the remaining liquid is more concentrated.

In countries of the temperate zone the sea water is concentrated by letting it evaporate spontaneously from a greatly enlarged surface. This is done by the "graduation" process (Fig. 53). Bundles of fagots are piled up together in a "rick," above which a trough with small outlet-holes runs from end to end. The brine is pumped up into the trough and trickles down from along the entire length of the latter upon the brush; in this way the surface of the salt solution is greatly enlarged and the evaporation is made much more rapid. A very concentrated brine flows out at the bottom.

The salt is obtained from this concentrated solution by boiling ("salt-boiling"). Common salt is almost equally soluble in hot and cold water, hence it does not crystallize out on cooling but falls out at the same rate as the saturated brine evaporates, even while boiling hot. The salt obtained from the first crystallization is of course impure, containing small amounts of magnesium salts, which render it hygroscopic. In order to purify it, it is redissolved in water and again precipitated by evaporation.

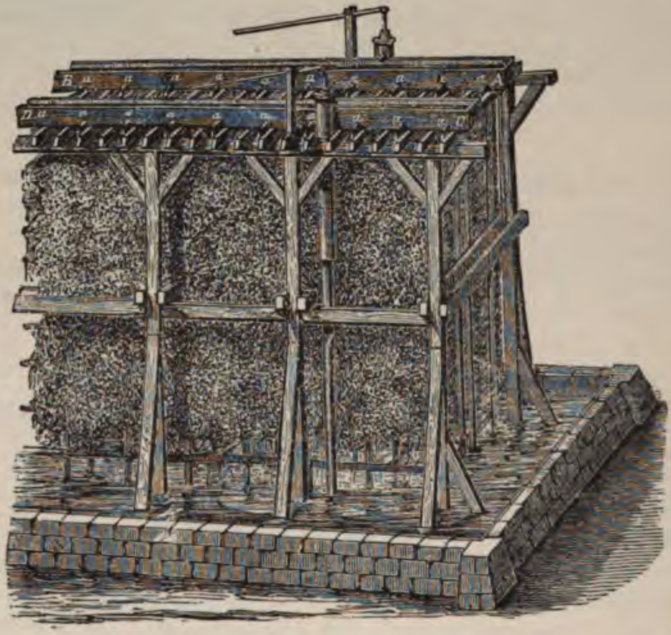


FIG. 53.—GRADUATION PROCESS.

Chemically pure sodium chloride is obtained by passing hydrochloric acid gas into a saturated solution of the salt or treating the solution with the concentrated acid. The sodium chloride is deposited because it is less soluble in hydrochloric acid than in water (§ 205).

Common salt crystallizes in cubes; when the solution evaporates slowly the well-known hollow four-sided pyramids, or hopper-crystals (Fig. 54), are formed. Sp. g. = 2.16. M.-pt. = 776°. 100 parts of water dissolve 36 parts NaCl at 0°. 39 parts at 100°; a saturated solution contains about 26% of salt. The crystals frequently enclose some of the mother-liquor; for this reason they decrepitate on heating. On cooling below −10° a saturated solution deposits crystals of the composition $NaCl+H_2O$, which lose their water at 0°. Chemically pure sodium chloride is not hygroscopic. It is insoluble in absolute alcohol.

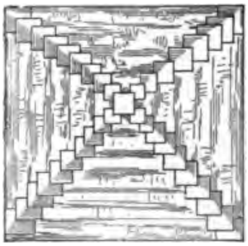


FIG. 54.—HOPPER-CRYSTAL OF SALT

Sodium bromide, NaBr, and **sodium iodide,** NaI, are more soluble in water than the chloride. From hot solutions they crystallize in anhydrous cubes, below 30° in monoclinic crystals with 2 mols. H_2O. Sodium bromide is difficultly soluble, sodium iodide easily soluble, in alcohol.

Sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$, is employed in photography (§ 247), in titrating iodine (§ 93) and as an antichlor (§ 82). It melts in its water of crystallization at 45° and forms supersaturated solutions very easily.

Sodium sulphate, $Na_2SO_4 \cdot 10H_2O$ (*sal mirabile Glauberi,* Glauber's salt—so called after the discoverer), can be obtained in various ways: (1) by heating common salt with concentrated sulphuric acid; (2) by conducting a mixture of air, sulphur dioxide and steam over hot sodium chloride (HARGREAVE's method):

$$2NaCl+SO_2+O+H_2O=Na_2SO_4+2HCl;$$

(3) by the double decomposition of magnesium sulphate and sodium chloride at a low temperature (winter-temperature):

$$MgSO_4+2NaCl=MgCl_2+Na_2SO_4.$$

This last process is carried out at Stassfurt, where large masses of magnesium sulphate occur.

At ordinary temperatures Glauber's salt crystallizes with ten molecules of water; above 33° it goes over into a mixture of water and anhydrous salt; below 33° the hydrous salt, $Na_2SO_4 \cdot 10H_2O$, is again formed. The system $Na_2SO_4 \cdot 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$ thus has a transition point at 33°. This is confirmed by the fact that the solubility of Glauber's salt in water suddenly changes at 33° from a rapid increase with rising temperature to a slow decrease.

This salt, like the preceding one, forms supersaturated solutions easily. The solution saturated at 33° can be cooled down to room-temperature without any deposition if care is taken to exclude even the tiniest crystal of the salt.

When a crystal of Glauber's salt is exposed to the air it *effloresces*, i.e., it gives off water vapor and becomes opaque, like chalk. This is evidently due to the fact that the vapor tension of its water of crystallization is greater throughout than that of the water vapor in the air. Inversely, we say that a salt *deliquesces* when it takes up water vapor from the air, as a result of the vapor tension of its saturated solution being less than the mean tension of the water vapor in the atmosphere. It is found that a perfectly sound crystal of $Na_2SO_4 \cdot 10H_2O$ does not effloresce, but that when efflorescence has begun at any point it spreads over the crystal. The phase rule gives a satisfactory explanation of this phenomenon. We have in the Glauber's salt two substances, Na_2SO_4 and H_2O; in the case of a perfectly bright crystal exposed to the air we have only two phases, $Na_2SO_4 \cdot 10H_2O$ and H_2O (moisture of the air). According to the equation $F+P=S+2$ (§ 71) we still have in this system two degrees of freedom, i.e., the pressure of the water vapor and the temperature can both be selected arbitrarily (within certain limits). If, however, some dehydrated salt is present, the number of phases is three; then there is only one degree of freedom, or, in other words, every temperature has only one corresponding pressure and inversely every pressure only one corresponding temperature. Accordingly it is only permissible to speak of the well-defined vapor tension of a salt with water of crystallization when a second solid phase is tacitly admitted to be present; for then only is the number of degrees of freedom reduced to one.

Glauber's salt is used in medicine; in the arts it is employed chiefly in the manufacture of soda.

Sodium nitrate, $NaNO_3$, called *Chili saltpetre* because of its extensive occurrence in Chili, crystallizes in rhombohedrons and melts at 318°. It is somewhat hygroscopic. Large quantities of it are used in fertilizing and also in the preparation of nitric acid and potash saltpetre.

Sodium nitrite, $NaNO_2$, is obtained by heating the nitrate, the addition of a reducing-agent such as lead or iron aiding the process. It is very soluble in water and is consumed in large quantities in the aniline-dye industry.

Sodium phosphates. (See § 146.) Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, is split up in aqueous solution chiefly into sodium hydroxide and the secondary salt, for the solution reacts strongly alkaline and absorbs carbonic acid from the air. The ordinary "sodium phosphate" is the disodium phosphate, $Na_2HPO_4 \cdot 12H_2O$. It separates from its aqueous solution at ordinary temperatures in large crystals which soon effloresce. 100 parts H_2O dissolve 9.3 parts of the salt at 20° and 24.1 parts at 30°. The solution is feebly alkaline. By leading in carbonic acid gas a liquid of amphoteric reaction (*cf.* § 224) is obtained, which turns blue litmus red as well as red litmus blue. Monosodium phosphate, $NaH_2PO_4 \cdot H_2O$, reacts acid. It is converted by heat into the metaphosphate.

226. Sodium carbonate, $Na_2CO_3 \cdot 10H_2O$ (*soda, sal-soda*), is, next to the chloride, the most important sodium salt and it is manufactured on an enormous scale. It occurs in nature in Egypt, in America (Wyoming), on the Caspian Sea, and elsewhere; the ashes of many marine plants contain it.

The *manufacture of soda* is carried on by three different methods:

(1) The LE BLANC soda process.

This process, which for a long period of years has practically controlled the industrial market, is now almost wholly superseded by the other two. The LE BLANC process consists of three parts. In the first place common salt is warmed with strong sulphuric acid (chamber-acid); hydrochloric acid and sodium sulphate (salt-cake) are formed:

$$2NaCl + H_2SO_4 = NaCl + NaHSO_4 + HCl;$$

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

In the second part of the process sodium sulphate is heated with coal and limestone, the following reactions taking place:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2;$$
$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

The third section of the process consists in lixiviating the mass last obtained ("black-ash") with water, whereby sodium carbonate is dissolved out. The latter is then obtained from this solution by crystallization.

(2) The ammonia-soda process of SOLVAY.

This process, which originally presented numerous technical difficulties, is now so perfected that it is rapidly displacing that of LE BLANC; in Germany already more than five-sixths of the total soda production is by the SOLVAY process. In England, however, the LE BLANC process is still most extensively used. The chemistry of the SOLVAY process is very simple. Ammonia and carbon dioxide are led alternately into a cold concentrated salt solution under pressure. The following reaction then takes place:

$$NaCl + (NH_4)HCO_3 = NaHCO_3 + NH_4Cl.$$

The acid sodium carbonate ("bicarbonate") so formed separates out, inasmuch as it is very difficultly soluble in the cold concentrated ammonium chloride solution. It is broken up, on heating, into soda and carbon dioxide, the latter of which is carried back to be used over. The ammonium chloride solution is distilled with lime or magnesia, whereby ammonia is recovered. The only waste-product, therefore, is chloride of calcium or chloride of magnesium, which can be worked up into hydrochloric acid or chlorine. Magnesium chloride, e.g., yields chlorine on heating in a current of air and is converted into magnesium oxide, which can be used anew in the decomposition of the ammonium chloride solution.

(3) Electrolytic Soda.

This process is based on the following actions: The electrolysis of an aqueous sodium chloride solution yields chlorine at the anode and hydrogen and sodium hydroxide at the cathode (see § 281). The anode is made of retort graphite because this is indifferent to the action of nascent chlorine; the cathode is made of iron. By using mercury instead of iron, sodium amalgam is formed, from which the mercury can be recovered by distillation. The sodium hydroxide which is the product of this action is converted into the carbonate by passing in carbon dioxide.

The apparently very simple process of electrolysis of a sodium chloride solution, expressed ordinarily by the equations

$$NaCl = Na + Cl \quad \text{and} \quad Na + H_2O = NaOH + H,$$

is in reality rather complicated. The resulting sodium hydroxide is itself an electrolyte and is broken up into sodium and hydroxyl ions. The sodium thus liberated immediately forms new hydroxide, but without increasing the alkalinity, since it was previously present as sodium hydroxide. The practical result, therefore, is a decomposition of water and consumption of electrical power proportional to the latter. Moreover the products of the electrolysis, sodium hydroxide and chlorine, interact forthwith, forming sodium hypochlorite. The hypochlorite diffuses in the solution and can be affected by the current in three ways: It can be split up by electrolysis, like every other salt of a oxy-acid, into base and acid with the evolution of detonating-gas; it can be reduced at the cathode to sodium chloride; and, thirdly, it can be oxidized at the anode to sodium chlorate. The latter, however, can itself be electrolyzed or reduced.

Sodium carbonate crystallizes at ordinary temperatures with ten molecules of water of crystallization in large transparent monoclinic crystals, which soon turn white and dull from loss of water (efflorescence). They melt at 60° in their own water; on continued warming the hydrate $Na_2CO_3 + 2H_2O$ is deposited; the latter loses one molecule of water in dry air and the remainder at 100°. At 30°-50° rhombic prisms of the composition $Na_2CO_3 + 7H_2O$ crystallize out of the aqueous solution. 100 parts H_2O dissolve 6.97 parts of the anhydrous salt at 0°, 51.67 parts at 38°. The aqueous solution reacts strongly alkaline (§ 184) because of hydrolysis. As was set forth in § 146, this phenomenon must always occur when a salt of a weak base and a strong acid or a salt of a weak acid and a strong base is formed. In case both acid and base are weak the hydrolysis will be all the greater. Which reaction the solution of such a salt will give depends on the relative strengths of the acid and base.

Soda is used commercially on a large scale, particularly in the soap and glass industries. It is the "washing-soda" of the household.

Acid sodium carbonate, $NaHCO_3$ (bicarbonate of soda), is obtained as a primary product in the SOLVAY process. It dissolves in 10–11 parts of water at room temperature and reacts alkaline. On being gently warmed it breaks up into carbon dioxide, water and soda; this decomposition occurs even on warming the aqueous solution, and when a current of air is passed through the concentrated solution at ordinary temperatures carbon dioxide escapes. It is used extensively in baking-powders and is the *saleratus* of commerce.

Sodium silicate (sodium water-glass) is prepared, among other ways, by fusing sand with Glauber's salt and charcoal. This yields a vitreous mass, which is dissolved by boiling water. The concentrated solution has the consistency of glue. It finds use as a fixative in calico printing, as well as for impregnating inflammable textiles like theater decorations, etc.; it is also used for "filling" soaps.

The **sulphides** of sodium correspond to those of potassium and are prepared in the same way (see § 231).

Sodium borate: *cf.* Borax (§ 283).

POTASSIUM.

227. Compounds of potassium occur in nature very extensively but not in such large quantities as those of sodium. Potassium exists principally in the silicates, especially feldspar and mica. Upon the decay of these minerals it is carried into the soil and thence into the plants, to which potassium compounds are indispensable. Potassium salts are also found in sea-water. The largest source of them, however, is the Stassfurt "*Abraum salts*" (§ 44), mainly double-salts of potassium and magnesium, such as *carnallite*, $MgCl_2 \cdot KCl \cdot 6H_2O$, *kainite*, $MgSO_4 \cdot KCl \cdot 3H_2O$, etc. The large amounts of potassium in the feldspars makes its recovery from them a very enticing problem.

The metal was first obtained by DAVY by the electrolysis of molten caustic potash. One of the commercial methods is to ignite a mixture of carbonate of potash and powdered charcoal (preferably charred acid potassium tartrate). The extraction of the metal is thus analogous to that of sodium; in the preparation of potassium, however, *potassium carbonyl*, $C_6(OK)_6$, may be formed under certain circumstances, a substance which acquires explosive properties on exposure to the air.

Potassium has a silvery-white metallic lustre and is almost as soft as wax at ordinary temperatures. Sp. g. =0.875 at 13°. It melts at 62.5° and boils at about 720°, forming a green vapor. The mirror-like surface of the metal immediately becomes dull in the air; when heated in the air it burns with an intense violet light. Water is decomposed by it with great vigor, the heat evolved being sufficient to ignite the escaping hydrogen and drive the piece of potassium around on the water.

Oxygen Compounds of Potassium.

228. Potassium oxide, K_2O, is formed by oxidizing thin shavings of potassium in dry air or by heating the peroxide with the metal. It is a white substance, which unites with water to form the hydroxide with the evolution of much heat.

Potassium peroxide, KO_2, is produced together with the monoxide on burning potassium in the air. It is dark yellow. In contact with water it yields potassium hydroxide, hydrogen peroxide and free oxygen.

Potassium hydroxide, KOH, results from the action of potassium on water and is generally prepared in the same manner as sodium hydroxide, viz., by treating potassium carbonate solution with milk of lime, $Ca(OH)_2$. It can also be obtained by heating saltpetre with powdered copper (forming copper oxide and potassium oxide), and adding water; the copper oxide can be removed by filtration. The hydroxide usually comes on the market in sticks.

The commercial product (" caustic potash ") is obtained chiefly by the first method and usually contains a little sulphate, chloride, etc., besides the carbonate which is gradually formed by the action of atmospheric carbon dioxide. It can be purified by treating with strong alcohol, which dissolves only the hydroxide; after filtering, the alcoholic solution is evaporated in a silver dish. Caustic soda is also purified in this way.

Potassium hydroxide is one of the strongest bases. In the solid state it greedily absorbs water and carbon dioxide from the air and finally deliquesces to a concentrated solution of potassium carbonate, while sodium hydroxide under these conditions turns to a solid white mass of soda. For this reason caustic potash is a much more suitable absorptive agent for carbon dioxide in analyses than caustic soda, for the use of the latter might easily cause a stopping up of the apparatus.

Caustic potash is used especially in the manufacture of soft soaps.

Potassium Salts.

229. **Potassium chloride,** KCl, occurs at Stassfurt in the mineral *sylvite.* It crystallizes in cubes and melts at 730°. It is easily volatilized at elevated temperatures. 100 parts H_2O dissolve 25.5 parts KCl at 0°, 57 parts at 100°. Like its sodium analogue, potassium chloride is precipitated from its saturated solution by hydrochloric acid. It unites with many salts to form double salts.

Potassium bromide, KBr, is important therapeutically. It is prepared by mixing bromine with a potassium hydroxide solution, the bromide and bromate being formed; the bromate is reduced by heating the salty product with powdered charcoal. Potassium bromide crystallizes in cubes and dissolves readily in water.

Potassium iodide, KI, also of medicinal value, can be prepared like the bromide and also in the following manner: Iodine and iron filings are mixed together under water, whereupon a solution of the compound Fe_3I_8 is formed; on treating this with a potash solution the oxide Fe_3O_4 is precipitated, carbon dioxide escapes and potassium iodide is left in solution; the salt is then obtained by filtration and evaporation. It crystallizes in cubes and is very soluble in water: 1 part H_2O dissolves 1.278 parts KI at 0°. On exposure to light or the air the crystals gradually turn yellow because of the separation of iodine.

It was remarked in § 46 that iodine, though only slightly soluble in water, dissolves to a much greater extent when the water contains potassium iodide. This is due to the formation of I_3' ions in the latter case. That the iodine has entered into combination may be concluded in the first place from the fact that the addition of iodine to an aqueous solution of potassium iodide does not cause a further depression of the freezing-point; the number of molecules is thus unchanged, or, in other words, iodine has combined with potassium iodide: in the second place, from the fact that carbon disulphide takes up nearly all the iodine from an aqueous solution of the latter when it is shaken with the solution, but only a small proportion when the same operation is performed with a solution of iodine in a dilute aqueous solution of potassium iodide. The distribution ratio for iodine between water and carbon disulphide is 1:410. If, therefore, we divide the concentration of the iodine in carbon disulphide by 410 we obtain the concentration of the *free* iodine in the potassium iodide solution. Subtracting this from the total concentration of the iodine in this solution, we have the amount of combined iodine. It is found that 1KI, or, rather, $1I'$, has taken up $1I_2$. I_3' ions are thus formed in the solution.

Nevertheless, a solution of iodine and potassium iodide in water behaves in many cases as if all the iodine were present in the free state, e.g. when it is titrated with sodium thiosulphate. This must be explained by the supposition that in the liquid we have the equilibrium:

$$I_3' \rightleftarrows I' + I_2.$$

If the free iodine is removed, the equilibrium is disturbed; a new portion of I_3' must therefore split up, and so on till it is entirely consumed.

Potassium fluoride, KF, possesses a peculiar property, which is lacking with the other halogen compounds of potassium: it combines with hydrofluoric acid eagerly, forming the double halide $KF \cdot HF$.

Potassium cyanide, KCN (often also written KCy), is manufactured on a large scale by fusing yellow prussiate of potash with potash:

$$K_4Fe(CN)_6 + K_2CO_3 = 5CNK + KCNO + CO_2 + Fe.$$

The cyanate of potassium KCNO is reduced by the iron to potassium cyanide also. It is very soluble in water, forming a strongly alkaline solution. On account of its great tendency to form double-salts, it is employed in electro-metallurgy. It is also used in extracting gold from its ores (§ 248).

Potassium chlorate, $KClO_3$, can be obtained by passing chlorine into a hot solution of caustic potash (§ 56). It is now prepared almost exclusively by the electrolysis of a hot solution of potassium chloride; however, it is more advantageous to first prepare sodium chlorate in this way, and then treat this with potassium chloride, because sodium chlorate is much more soluble and does not retard the electrolytic process by separating from the solution, as does potassium chlorate.

Potassium chlorate is a well-crystallized salt, which is used for the preparation of oxygen (§ 9); furthermore, it is used in the manufacture of matches and fireworks, and also medicinally as a remedy for sore throat. On being heated it gives up oxygen, part of the salt being at the same time converted into **potassium perchlorate,** $KClO_4$.

The last-named salt is difficultly soluble in water. It is sometimes found in crude Chili saltpetre, rendering the latter unfit for use in fertilizing various cultivated plants.

Potassium sulphate, K_2SO_4, is obtained by the action of sulphuric acid on potassium chloride. It crystallizes in beautiful, lustrous rhombic prisms and dissolves with some difficulty in cold water (1 part in 10 parts H_2O at room temperature). It is used principally for the preparation of potash according to the LE BLANC method. **Acid potassium sulphate,** $KHSO_4$, is very soluble in water; it melts at 200°, losing water and going over into **potassium pyrosulphate,** $K_2S_2O_7$. The latter breaks up into potassium sulphate and sulphur trioxide on heating.

Potassium nitrate, KNO_3, is widely distributed in nature,—although usually found only in small amounts,—for it is formed wherever nitrogeneous organic bodies decay in contact with potassium compounds. This is the basis of an artificial method of preparing saltpetre, which method was formerly much used.

Another process of manufacture depends on the double decomposition of Chili saltpetre with potassium chloride, which is obtained in large quantities at Stassfurt:

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

For this purpose hot-saturated solutions of the two salts are brought together. As sodium chloride is much less soluble than saltpetre at the temperature of boiling water, it is the first to crystallize out on evaporation, but when the solution is cooled the saltpetre comes out first, for it is much less soluble than sodium chloride in cold water.

Potash saltpetre crystallizes in anhydrous prisms, either rhombohedral or rhombic according to the temperature. In the neighborhood of the melting-point the former is the stable variety, at ordinary temperatures the latter. The location of the transition point of the two forms has not yet been determined. 100 parts H_2O dissolve 13.3 parts KNO_3 at 0°, 247 at 100°. It melts at 338°; farther heating breaks it up into potassium nitrite and oxygen. It has a cooling taste.

230. Potash saltpetre is consumed in large quantities in the manufacture of *gunpowder*. This is a mixture of sulphur, charcoal and potash saltpetre, the proportions varying in different countries, but being in most cases 75% KNO_3, 10% S and 15% charcoal.

These proportions of the three ingredients correspond very closely to 2 molecules KNO_3, 1 atom S, and 3 atoms C, which would call for 74.8% KNO_3, 11.8% S and 13.4% C. One might therefore be inclined to express the decomposition of gunpowder, in the main, by the equation:

$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2.$$

The chemical reactions which come into play in the explosion of gunpowder are really much more complex, however. **Abel** and **Nobel** have investigated the products formed when it explodes under conditions analogous to those in firing a gun. They found that about 55–58% of solid matter remains, i.e., about 45–42% goes off as gas. The solids are at least half potash, while potassium sulphate and thiosulphate also are found in considerable quantities. The gases are chiefly carbon dioxide and nitrogen, and carbon monoxide in a smaller quantity. The tension of the gaseous products amounted to about 6400 atmospheres and the temperature attained was about 2200°.

The solid products of the combustion of gunpowder become very finely divided as a result of the explosion and remain suspended in the air for a long time as smoke. Gunpowder (black powder), which was formerly the only explosive material in use, is now being supplanted more and more by *smokeless* powder. This consists of organic substances which yield only gaseous products on exploding, and hence there is no smoke. (See Org. Chem., § 231.)

231. Potassium phosphates.—The three potassium salts of phosphoric acid are known. They are very soluble in water.

Potassium carbonate, K_2CO_3, *potash*.—This salt was formerly obtained solely from wood-ashes, these being soaked in water and the strained liquor evaporated. At present it is manufactured extensively from potassium chloride after the LE BLANC process. Another source of potash is the molasses of the beet-sugar factories, that contains the potassium salts in which the sugar-beet is rich.

At the Neustassfurt salt mine it is made from potassium chloride by a patented process as follows: Magnesium carbonate, $MgCO_3 \cdot 3H_2O$, is suspended in a solution of potassium chloride, and carbon dioxide is led in, whereupon the following reaction takes place:

$$3MgCO_3 \cdot 3H_2O + 2KCl + CO_2 = MgCl_2 + 2MgCO_3 \cdot KHCO_3 \cdot H_2O.$$

The potassium magnesium carbonate separates out and is broken up by heating to a temperature not exceeding 80° into magnesium carbonate and potash. The former salt is again obtained with three molecules of water of crystallization, which form is the only one suited for the above reaction.

Potassium carbonate is a white powder, which deliquesces in the air and is very soluble in water (1.12 parts K_2CO_3 in 1 part H_2O at 20°); the solution has a strong alkaline reaction. The salt melts at 838°. It is used in the preparation of soft soaps and hard glass (potash-glass).

Potassium silicate, potassium water-glass, is formed when sand is fused with potash. Different salts of this sort are described. They dissolve in water, forming a thick, mucilaginous mass which on drying turns to a vitreous, and finally opaque, product. Potassium water-glass is used for the same purposes as sodium water-glass.

Sulphides of Potassium.

Potassium monosulphide, K_2S, is prepared by reducing potassium sulphate with charcoal. It dissolves in water very readily and crystallizes out with five molecules of water. It absorbs oxygen from the air, going over into the thiosulphate and hydroxide:

$$2K_2S + H_2O + 2O_2 = K_2S_2O_3 + 2KOH.$$

Acids react with it, liberating hydrogen sulphide.

Potassium hydrosulphide, KSH, is obtained by saturating a caustic potash solution with hydrogen sulphide:

$$KOH + H_2S = KSH + H_2O.$$

It is very soluble in water, the solution reacting alkaline; on evaporation *in vacuo* the solution deposits crystals of the composition $2KSH + H_2O$. With potassium hydroxide it forms the monosulphide:

$$KSH + KOH = K_2S + H_2O.$$

Potassium polysulphides.—When a solution of potassium monosulphide is boiled with sulphur, we obtain the compounds K_2S_3, K_2S_4, K_2S_5. A mixture of these substances is also obtained by fusing potash with sulphur; besides these it contains the sulphate and the thiosulphate and is called *hepar sulphuris* ("liver of sulphur") because of its liver-brown color. These polysulphides are decomposed by acids with the evolution of hydrogen sulphide and the separation of sulphur:

$$K_2S_x + 2HCl = 2KCl + H_2S + (x - 1)S.$$

Rubidium and Cæsium.

232. These elements are widely distributed, but always occur in extremely small amounts. The silicate *lepidolite*, or lithia mica, frequently contains a little rubidium. The exceedingly rare mineral *pollux* from the isle of Elba is a silicate of aluminium and cæsium, and contains about 30% cæsium oxide. In general these elements are found wherever potassium salts are met with: in mineral springs, in the Stassfurt salts (*carnallite* contains rubidium), etc. They were discovered by BUNSEN and KIRCHHOFF in 1860 with the aid of spectrum analysis (§ 264) and obtained their names from the most important lines in their spectra (*rubidus* = dark red; *cæsius* = sky-blue).

In order to separate them from the large amount of potassium salts with which they generally occur, they are converted into chlorides and the solution is evaporated, whereupon the dry residue is extracted with strong alcohol. Almost all the sodium chloride and potassium chloride remains behind, while the chlorides of rubidium and cæsium dissolve. Platinum chloride is then added to precipitate K_2PtCl_6, Rb_2PtCl_6, and Cs_2PtCl_6; the solubility of these double salts in water is quite different (at 10° 100 parts H_2O dissolve 0.9 parts K_2-salt, 0.154 Rb_2-salt, and 0.05 Cs_2-salt), so that they can be very well separated by fractional extraction with boiling water. The rubidium iron "alum" is particularly well suited for the purification of rubidium salts, and especially for their separation from potassium salts, since it is readily soluble in hot, and only slightly soluble in cold, water and moreover crystallizes beautifully; potassium iron alum, on the other hand, is very soluble even in cold water.

The metals rubidium and cæsium are best obtained by heating their hydroxides with magnesium powder in an iron pipe. Rubidium has a silvery lustre, melts at 38.5, and has a specific gravity of 1.522 at 15°. The metal oxidizes very rapidly in the air or in oxygen, forming dark brown crystals of the peroxide, RbO_2. On being heated in a current of hydrogen it yields the hydroxide and free oxygen:

$$2RbO_2 + 2H_2 = 2RbOH + H_2O + O.$$

The hydroxide is a very strong base; its salts show much similarity to the analogous potassium compounds; they are in several instances less soluble, e.g. Rb-alum, Rb-perchlorate (§ 60), etc.

Cæsium is a silvery-white metal; sp. g. 1.85; m.-pt. 26.5°; b.-pt. 270°. It soon takes fire on exposure to the air. The salts of cæsium are very similar to those of rubidium; some of them are even less soluble, and are therefore used for the preparation of pure cæsium compounds. This is particularly true of the platinum double-salt already mentioned and the cæsium alum and the acid tartrate.

Rubidium bromide and iodide, and even more so the corresponding compounds of cæsium, have the property of combining with two atoms of bromine and iodine, forming yellow or brown crystalline compounds, e.g. CsI_3; these metals can thus be trivalent.

SUMMARY OF THE GROUP OF ALKALI METALS.

233. The gradual change of the physical properties of these metals with increasing atomic weight is made plain by the following table:

	Li	Na	K	Rb	Cs
Atomic weight.	7.03	23.05	39.15	85.4	133.
Specific gravity.	0.59	0.97	0.865	1.52	1.85
Melting-point.	180.0°	97.6°	62.5°	38.5°	26°–27°
Boiling-point.	Red heat	742°	667°	.. ..	270°
Atomic volume	11.8	23.7	45.3	56.7	71.9

The specific gravity increases with the atomic weight, as does also the atomic volume; on the other hand, there is a fall in the melting- and boiling-points.

From a chemical standpoint we notice, in the first place, the same general type in the compounds, showing that all these elements are univalent. The hydroxides all have the formula ROH, the halogen compounds RX, etc. The salts of them all, even the carbonates and phosphates, are soluble in water (although in different degrees), the carbonates with basic reaction. The metals all oxidize very readily in the air.

On the other hand, we cannot overlook the fact that the metals potassium, rubidium and cæsium, which are very similar to each other, differ from sodium and lithium in many respects. The last-named metal, as we shall see in the sequel, displays analogy with magnesium in several important points, thus differing from the metals of its own group. A slight divergence in the behavior of the first members of a group from that of the rest is found to characterize almost all of the groups. We may recall carbon, for instance, the first member of the fourth group, which differs distinctly from silicon and the rest in the ability of its atoms to unite with each other; also fluorine with its soluble silver compound. Still other examples of this sort will be met with later.

Sodium differs from the sub-group, K, Rb, Cs, in the solubility of its salts. The sodium salts are almost all readily soluble in water; this is true even of the platinum double-salt, Na_2PtCl_6, the acid sodium tartrate and others. Soda crystals effloresce, while potash deliquesces in the air. The spectra of sodium, on the one hand, and the other alkali metals, on the other, are entirely dissimilar.

Ammonium Salts.

234. In the description of ammonia (§ 112) it was already observed that it combines with acids directly, forming salts which are very similar to those of potassium, and in which the group, NH_4, the *ammonium* group, is assumed to exist. In connection with the alkali group a description of a few ammonium salts may find a place.

The aqueous solution of ammonia must, because of its electrical conductivity and its alkaline reaction, contain $NH_4^{\cdot}$ and OH' ions and hence also undissociated molecules of ammonium hydroxide, NH_4OH. While solutions of the alkalies, KOH, NaOH, etc., conduct the electric current very well, this is not the case with an ammonia solution; it is a poor conductor. A 0.1 normal solution contains only 5% of ionized NH_4OH molecules, while a solution of potassium hydroxide of the same concentration is 91% ionized.

An aqueous solution of ammonia may be presumed to contain: (1) free ammonia, NH_3; (2) hydrates of ammonia, $NH_3 \cdot n$ aq.; (3) ammonium hydroxide, NH_4OH; (4) the ions $NH_4^{\cdot}$ and OH'. The existence of these hydrates in addition to free ammonia reveals itself in the behavior of ammonia solutions on being shaken with chloroform. According to BERTHELOT's law (ORG. CHEM., § 25) the distribution ratio of the ammonia between the two solvents should be constant. But this is not the case. Therefore, just as the deviations from HENRY's law lead us to conclude that a dissolved gas exists in a special condition, so we can apply a similar explanation to the exceptions to the BERTHELOT law; for HENRY's law is really the expression of the distribution ratio of a gas between a liquid and a vacuum, while the other law has to deal with the distribution ratio between two liquids.

Since in the case of ammonia this deviation is observed only when one of the two liquids is water, we are obliged to conclude that there is a combination of the ammonia with the water. The reason for assuming the existence of hydrates instead of ammonium hydroxide, NH_4OH, is a double one. We have, on the one hand, the analogy between the behavior of ammonia and amines and, on the other, the entirely abnormal behavior of the organic quaternary ammonium bases. For, while the aqueous solutions of primary, secondary and tertiary amines are weak electrolytes, as is the case with ammonia, the solution of a quaternary base, on the contrary, conducts electricity as well as a solution of potassium or sodium hydroxide. We may thus conclude that if ammonium hydroxide, NH_4OH, could reach the same concentration in solution as a quaternary base it would display just as great a conductivity as the latter. Unlike the quaternary base, however, it breaks up principally into ammonia, NH_3, and water, for the quaternary base cannot be thus decomposed.

That an aqueous ammonia solution really contains at least an appreciable quantity of the hydroxide is evidenced by the existence of its ions. These necessitate the establishment of the equilibrium

$$NH_4OH \rightleftarrows NH_4^{\cdot} + OH',$$

however far the point of equilibrium may be displaced toward the right.

The great tendency of ammonium hydroxide to break up into ammonia and water is the reason for the very feeble basic reaction of an aqueous solution of ammonia, for undoubtedly ammonium hydroxide, so far as it is formed, is extensively ionized, like the strong bases. This view is supported by various observations, among them the neutral reaction of the ammonium salts of strong acids, such as the chloride and the nitrate, and also the alkaline reaction of the carbonate and the cyanide, in harmony with the similar alkaline reaction of the corresponding salts of the alkali metals.

Ammonium chloride, NH_4Cl, *sal ammoniac,* is obtained from the ammonia liquor of the gas factories (§ 112). The ammonia is expelled by warming and absorbed in hydrochloric acid; this solution is evaporated and the solid residue sublimed, whereby the salt is obtained in compact fibrous masses. It dissolves in 2.7 parts of cold, and in 1 part of boiling, water and crystallizes out of the solution in small, usually feather-like groups of octahedrons or cubes. It has a sharp saline taste.

Ammonium chloride vaporizes easily, dissociating into ammonia and hydrochloric acid, as is shown by the vapor density, which at 350° is only half as great as calculated.

This dissociation can be easily demonstrated in the following manner: Introduce into a tube sealed at one end a little ammonium chloride and, not far from this, a piece of blue litmus paper. In front of the latter is pushed a plug of asbestos wool and finally a piece of red litmus paper. The chloride is then heated. Since hydrochloric acid has a smaller diffusion velocity than ammonia the latter passes through the wad first and colors the red paper blue; as a result an excess of hydrochloric acid is left at the other end and it reddens the blue paper placed there.

It is a remarkable fact, discovered by Baker, that perfectly dry ammonium chloride (having stood for a long time in a desiccator over resublimed phosphorus pentoxide) has the normal vapor density. On the other hand, the same investigator found that similarly dried ammonia gas and hydrochloric acid gas do not unite to form ammonium chloride (§ 38). Traces of water thus produce a marked catalytical acceleration, both of the formation and of the decomposition of ammonium chloride. We have here an illustration of the general rule that when one part of the system in a reversible reaction is accelerated by a catalyzer the other must be likewise affected. The proof of this rule lies in the impossibility of the contrary being true, since that would necessitate a change in the equilibrium (see § 49).

In many other cases it is also observed that traces of water have a considerable influence on the velocity of chemical reactions. The following examples may be cited: (1) Phosphorus, that ordinarily takes fire in moist air at a little above room temperature, can be heated in oxygen to 150° without ignition, provided the oxygen has been carefully dried by phosphorus pentoxide. (2) Carbon monoxide burns in moist oxygen much more easily than in dry oxygen. (3) Very carefully dried detonating-gas can be heated in a tube to red-heat without exploding.

Ammonium sulphate, $(NH_4)_2SO_4$, crystallizes in large rhombic prisms and dissolves very readily in water. On boiling the aqueous solution some ammonia escapes, acid sulphate being formed.

Its solution in 30% hydrogen peroxide yields on evaporation crystals of the composition $(NH_4)_2SO_4 \cdot H_2O_2$. When these are heated under reduced pressure a high per cent hydrogen peroxide distils off.

Ammonium nitrate, NH_4NO_3, deliquesces in the air; when heated it breaks up into water and nitrous oxide (§ 119). This salt is known in three crystallized modifications, the transition points (§ 70) of which have been determined.

Ammonium phosphates.—The tertiary salt, $(NH_4)_3PO_4$, is deposited in crystalline form on mixing concentrated solutions of phosphoric acid and ammonia. It cannot be dried, however, for it then loses ammonia and goes over into the secondary phosphate, $(NH_4)_2HPO_4$. On boiling the solution the salt again yields ammonia and is transformed into the primary phosphate.

The best known of these salts is the **sodium ammonium phosphate,** $NaNH_4HPO_4 \cdot 4H_2O$, *microcosmic salt*. It forms large transparent crystals. On being heated it melts, loses water and ammonia, and passes over into a vitreous substance, sodium metaphosphate, $NaPO_3$.

Ammonium carbonate was formerly obtained by the dry distillation of nitrogenous organic substances, such as hair, nails, leather, etc., hence the name "salt of hartshorn," which still clings to it. At present, however, it is made by dry distilling a mixture of calcium carbonate and ammonium chloride or sulphate. The product is a mixture (molecule for molecule) of acid salt, NH_4HCO_3, and ammonium carbamate, $NH_2 \cdot CO_2 \cdot NH_4$ (this latter being the neutral salt minus $1H_2O$). From its composition, $(NH_3)_3(CO_2)_2 \cdot H_2O$, it takes the name *ammonium sesquicarbonate*, On passing ammonia gas into a concentrated aqueous solution of it the neutral salt, $(NH_4)_2CO_3$, separates out as a crystalline powder; it smells strongly of ammonia and passes slowly over into the acid salt, NH_4HCO_3, a white odorless powder, which is scarcely soluble in water. This acid salt is also formed directly from the sesquicarbonate, as the latter gives off carbon dioxide and ammonia in the air (hence the odor of ammonia) and goes over into the first-named salt.

Ammonium sulphide is extensively used in analysis (§ 73). A solution of ammonium hydrosulphide (or sulphydrate), NH_4SH, is obtained by saturating aqueous ammonia with hydrogen sulphide; it is a colorless liquid, which soon turns yellow because of the formation of ammonium polysulphides. The oxygen of the air oxidizes part of the hydrogen sulphide and thus sets free sulphur, which combines with ammonium hydrosulphide to form polysulphides. These polysulphides are also obtained by dissolving sulphur in a solution of ammonium hydrosulphide.

On mixing 2 vols. NH_3 gas and 1 vol. H_2S gas at $-18°$ a white crystalline mass is obtained, which decomposes at ordinary temperatures into NH_4SH and NH_3. The compound NH_4SH separates out crystalline when hydrogen sulphide is passed into alcoholic ammonia. As low as 45° it is completely dissociated into equal volumes of NH_3 and H_2S.

SALT SOLUTIONS.

235. Every solid substance is soluble in every liquid; however, the proportion which dissolves can vary all the way from zero to infinity. If only an infinitesimal amount of the solid goes into solution, we say ordinarily that the substance is " insoluble " in the liquid; there can be no doubt, however, that, if our means of investigation were sufficiently improved and large enough quantities of liquid were taken, the solubility would be perceptible. This has already been demonstrated in many cases of so-called insoluble substances (§ 210). Even when we confine our attention to aqueous solutions of salts (including acids and bases) we find the same infinite difference in solubility that is observed between substances in general. Substances such as sand, barium sulphate (§ 262), silver iodide, etc., are "insoluble"; others like sulphuric acid are able to dissolve in any given amount of water.

The solubility, i.e. the maximum relative amount of salt that can go into solution, is a function of the temperature and the pressure. In the great majority of cases the solubility increases with the temperature. If the temperature is plotted on the axis of abscissas and the amount of salt which dissolves in one hundred parts of water is plotted on the ordinate axis, a *solubility curve* is obtained (Fig. 55) which shows at a glance the variation of the solubility with the temperature.

For some salts, e.g. potassium nitrate, the solubility increases very rapidly with the temperature; for sodium chloride it remains practically constant. In certain cases, such as those of calcium hydroxide and calcium sulphate (within certain limits of temperature) the solubility decreases with rising temperature. These phenomena are connected, as has already been explained, with the *heat of solution*, i.e. with the caloric effect which accompanies the process of solution, and in the manner expressed by VAN'T HOFF's principle of mobile equilibrium (§ 103). In fact saltpetre, for instance, whose solubility increases very rapidly with the temperature (see Fig. 55) dissolves in water with a considerable absorption of heat.

236. The term *heat of solution* has various meanings. We are obliged to distinguish between (1) the caloric effect of dissolving a salt in a very large amount of water; (2) the caloric effect of dissolving a salt in an almost saturated solution; and (3) the total heat of solution, i.e. the whole caloric effect of dissolving a salt in water until the solution is saturated. As a rule these three magnitudes will have dissimilar values, indeed their algebraic signs may be opposite. This is the case, for instance, with the compound $CuCl_2 \cdot 2H_2O$; 1 g.-mol. dissolved in 198 g.-mols. H_2O at 11° gives a caloric effect of $+3.71$ Cal.; 19.56 g.-mols. in the same amount of water, -3.129 Cal.

The heat of solution to which VAN'T HOFF's principle applies is that of the salt in its saturated solution. We have here the system: salt + saturated solution; when the temperature changes, the equilibrium is displaced, i.e. salt either goes into solution or crystallizes out, the latter action producing just as large a thermal effect numerically as dissolving in the saturated solution, but with the opposite sign. Since this was not taken into consideration when the matter was first dis cussed, it was believed that there were exceptions to the principle, but closer investigation has proved the contrary.

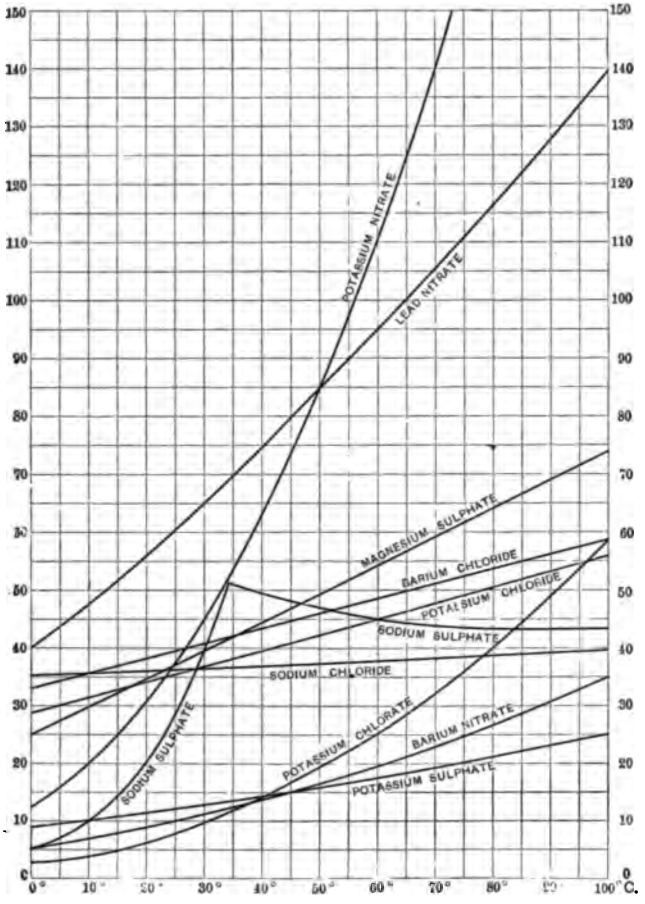


FIG. 55.—SOLUBILITY CURVES.

In some cases the solubility of a salt at first increases gradually with rising temperature and then steadily decreases, so that the solubility curve has a maximum (*cf.* Fig. 56). In full agreement with VAN'T HOFF'S principle the heat of solution is negative in the ascending portion of the curve, zero at the maximum and positive in the descending portion. In the case of gypsum, $CaSO_4 \cdot 2H_2O$, for instance, the maximum was found to lie at about 38° and at that point the heat of solution was actually proved to be 0.00; at 14° it is −0.36; above 35°, +0.24.

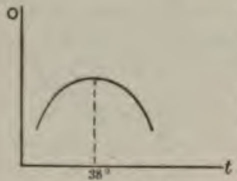


Fig. 56.

The effect of pressure on the solubility is at the most very slight, but it is in entire accord with the principle of Le Chatelier. Ammonium chloride, for instance, dissolves with expansion; therefore its solubility lessens with increasing pressure (1% for an increase of 160 atm.). Copper sulphate, which dissolves with contraction, has its solubility increased 3.2% by an increase of 60 atm. pressure.

237. It was formerly thought that the terms "solvent" and "dissolved substance" ("solute") should be kept distinct. However, it has since developed that there is no essential difference between the components of a solution, and that aqueous solutions are therefore better defined as "liquid complexes, one of whose components is water," than as "water in which substances are dissolved."

The interchangeability of the terms "solvent" and "solute" is evidenced first of all by the phenomena attending the cooling of salt solutions. Let us consider, for instance, a nearly saturated solution of potassium chloride at a definite temperature. We have in it two substances (KCl and H_2O) and two phases (§ 71), hence two degrees of freedom. We will suppose that the solution is then cooled; potassium chloride crystallizes out forthwith and, as three phases are then present, the system becomes univariant We recall that changes in the quantity of any phase have no effect on such a system; therefore, if more salt is introduced into the system, the concentrations of saturated solution and vapor are unaffected. This is none the less true when water is added or the vapor volume increased, so long as the three phases remain.

On cooling still farther, more potassium chloride is gradually deposited until a point is reached below which the entire liquid congeals to a mixture of salt and ice. This point is known as the **cryohydric,** *or* **eutectic, point**. There are now four phases,—salt, ice, solution and vapor;—hence the system has become nonvariant.

The opinion was formerly held that at this point a chemical compound between the salt and water (a "cryohydrate") came into existence. That it is only a matter of mixtures can be seen in the case of colored salts (K_2CrO_4), for instance, with a microscope; moreover the composition of these so-called hydrates may differ in case the solidification takes place under a different pressure.

If we start with a dilute potassium chloride solution as another example, and cool it, we have ice formed at a definite temperature and a univariant system established, ice being the third phase required. Below this point *the solution can be regarded as saturated in respect to ice,* just as it could be considered saturated in respect to the salt in the previous case; for an increase of the solid phase (ice) does not now cause a displacement of the equilibrium (§ 71) any more than the addition of the solid (salt) did in the previous instance. The addition of potassium chloride causes part of the ice to go into solution (i.e. melt); for the dissolving of more salt increases the concentration of the solution. Therefore, if the temperature is kept constant, ice must melt in order to restore the solution to its previous concentration. It is therefore perfectly analogous to the addition of water to a saturated potassium chloride solution in contact with the solid salt, in which case also the solid phase goes into solution. If the temperature rises, more ice dissolves; if it falls, more crystallizes out—just as with rising temperature more potassium chloride goes into solution and with sinking temperature more crystallizes out. On farther cooling more and more ice will be deposited until, in this case also, the cryohydric point is reached, below which the whole system solidifies to a mixture of salt and ice. The analogy is therefore complete.

The cryohydric point is, according to this view, the point of intersection of two curves, viz.: the solubility curves of salt and of ice in the salt solution.

Another argument against the assumption of any essential difference between solvent and solute is found in the behavior of the solutions of certain hydrous salts, e.g. $CaCl_2 \cdot 6H_2O$. A saturated solution of $CaCl_2$ in water at 30.2° has exactly the composition $CaCl_2 \cdot 6H_2O$. At this temperature, therefore, the hydrate melts to a homogeneous liquid. *If either H_2O or $CaCl_2$ is added, there is a deposition of $CaCl_2 \cdot 6H_2O$ on cooling,* for the addition of either causes a depression of the point of solidification (freezing-point) of $CaCl_2 \cdot 6H_2O$. In the first case this hydrate is in equilibrium with a liquid which contains more water than the hydrate does and which is therefore called an aqueous solution in the ordinary sense. In the second it is in equilibrium with a liquid which contains more $CaCl_2$ than $CaCl_2 \cdot 6H_2O$ and must therefore be regarded as a solution in $CaCl_2$.

On examining the solubility curves of various salts (*cf.* Fig. 55) it is found that they are in general regular; however, in one of the curves (sodium sulphate) a sudden change of direction is noticed. This is often observed with salts that contain water of crystallization. Taking sodium sulphate as an example, the phenomenon may be explained thus: It has already been remarked (§ 225) that this salt has a transition point at the temperature of 33°, $Na_2SO_4 \cdot 10H_2O$ being transformed into Na_2SO_4 and $10H_2O$. Up to 33°, therefore, we have the hydrous salt as the solid phase; above this temperature the anhydrous salt. This change must necessarily involve a sudden bend of the solubility curve. Below 33° the curve represents the solubility of $Na_2SO_4 \cdot 10H_2O$, above 33° that of Na_2SO_4. We can therefore also *regard the point of inflection of the curve (at 33°) as the point of intersection of the curves for $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4.* In sodium sulphate the special case appears where the solubility of the anhydrous salt decreases with rising temperature and hence the solubility curve falls as the temperature rises above 33°.

In the light of the above the solubility of a substance which has a transition point is the same for both modifications at this point. This must always be the case; it can be demonstrated in the same way as in § 70, where it was shown that the vapor pressures become equal at the transition point. Indeed the same figure can be employed, if it is borne in mind that the solubility of a metastable modification is always greater than that of the stable modification at one and the same temperature. Inversely, moreover, we have here a means of determining the transition point.

In general, as OSTWALD has pointed out, the solubility of any substance whatever is dependent on the condition in which it exists. The solid phase determines the equilibrium, not only in virtue of its chemical composition but also by the particular modification in which the solid substance is present. Thus, e.g., each of the various forms of the same polymorphous substance or different hydrates of the same salt has its own solubility, other things being equal.

In a hydrous salt we may have the case where there are various hydrates, which are connected with each other by transition points. A salt with $m+n$ molecules of water of crystallization passes over at a definite temperature into another with m molecules, for example. The latter may, at a higher temperature, have a second transition point (to anhydrous salt). At each of these points the solubility curve will show a bend, because the solid phase changes; the curve will therefore assume some such form as that of Fig. 57.

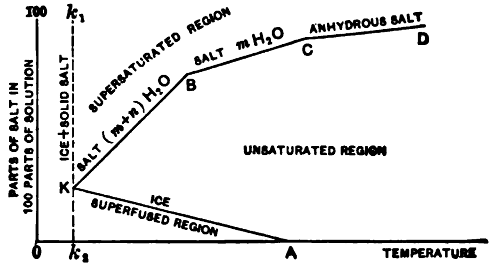


FIG. 57.

Let us examine such a solubility curve a little more closely. At 0° (A in Fig. 57) we will suppose that we have pure water and ice, to start with, and that small portions of salt are then gradually dissolved. If the ice phase is to be preserved, the temperature must be allowed to sink, for a salt solution has a lower freezing-point than pure water. We therefore move along the curve AK. Soon a point K is reached when no more salt dissolves, since all the water has now turned to ice. Here, therefore, we have a mixture of ice and solid salt, or, in other words, the cryohydric point.

If we wish to bring more salt into solution after K is reached the temperature must be raised. The ice phase then, of course, disappears and in its place we have the salt with $m+n$ molecules of water of crystallization as solid phase. If the temperature is steadily raised and the solution is kept constantly saturated by the addition of this salt, we move along the curve KB. At B, however, we meet the transition point from the salt with $m+n$ mols. H_2O to the one with m mols. H_2O; hence the solubility curve must again bend here and in such a way that at the point B the solubility curve of the salt with $m+n$ mols. H_2O is steeper than that of the salt with m mols., no matter what the form of the curves KB and BC may be. This is readily understood by a course of reasoning entirely analogous to that given for the transition of ice to water or of rhombic to monoclinic sulphur (§ 70). Finally at C we have a second transition point from salt with m mols. H_2O to anhydrous salt, so that the solubility curve there shows one more bend. Where the curve CD ends depends on circumstances. In many cases, e.g. that of silver nitrate, it ends at the melting-point of the anhydrous salt (concentration of the solution $=100\%$). In other instances the anhydrous salt can form a second (fused) liquid layer under the saturated solution. Finally, mention may also be made of the case of copper sulphate, which at a given temperature loses its water of crystallization in contact with its saturated solution and from that point on shows a decrease in solubility with rising temperature, which finally ends in almost total insolubility.

If we draw a line k_1k_2 through K parallel to the ordinate axis, the figure is divided by this line and $AKBCD$ into the following regions: To the right of the solubility curve is the region of the unsaturated solutions, AKk_2 is that of the superfused, k_1KBCD that of the supersaturated, solutions. To the left of k_1k_2 only ice + solid salt can exist under ordinary pressures.

A solubility curve, such as that represented in Fig. 57, can, on the other hand, be used to detect the existence of compounds between the salt and the water. From the cryohydric point upward every bend in the solubility curve shows that a salt with a different amount of water of crystallization has been formed. Each branch of the curve thus represents a separate salt, i.e. a different solid phase. The composition of these solid phases is by no means always self-evident. Such is, however, the case when the phase fuses without altering its composition, or, what amounts to the same thing, when it can exist in equilibrium with a liquid phase of the same composition. This does not often occur with salts in aqueous solution, but an example of it was seen above in the case of $CaCl_2 \cdot 6H_2O$. The inspection of the solubility curve or melting-point curve is then especially valuable for the discovery of compounds. In order to understand this let us first examine a system of two substances, A and B, which do *not* combine. Fig. 61 represents the melting-point curve that one obtains on the addition of increasing amounts of B to A. At first the melting-point sinks until the eutectic point * *E* is reached. Along *AE* A alone separates out of the fused mass on freezing. At *E*, however, B also separates out. If more of B is now added the melting-point rises; we obtain the curve *EB*, which terminates in the melting-point of pure B. Along *EB* only B separates out of the fused mass.

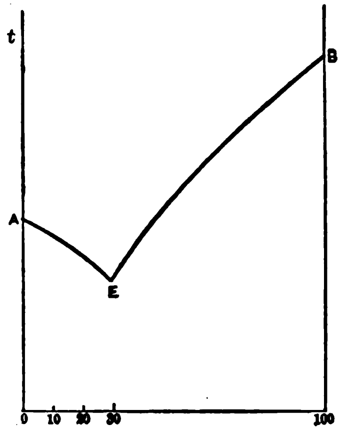


FIG. 58.

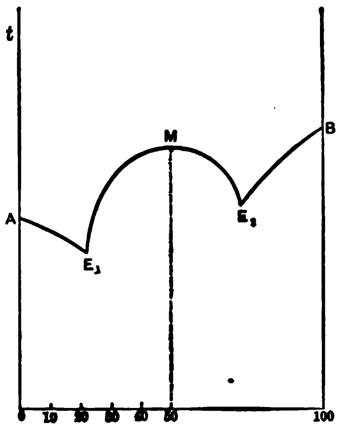


FIG. 59.

Suppose we now assume that A and B form a compound AB in the molecular proportions 1:1 (Fig. 59). On the addition of B to A AB is formed and dissolves in the excess of A. This lowers its melting-point. When a certain amount of B has been added this point is lowered to E_1. Here both A and AB separate out. E_1 is the eutectic point for mixtures of A and AB. If more of B is added the melting-point rises, just as in the case where there is no combination between the components. Only AB now separates out of the fused mass. The continued addition of B, however, increases the amount of the compound AB; at *M* free A has disappeared and the mass consists wholly of pure AB, whose melting-point is *M*. At this point the melting-temperature reaches its maximum, for the addition of either A or B lowers the melting-point of the pure compound. The further course of the curve is readily seen. As more and more B is added to AB the melting-point sinks, AB alone separating out, until the eutectic point E_2 is reached, where both AB and B crystallize out, and thereafter the melting-point again rises along E_2B till it finally ends in the melting-point of the pure substance B.

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* The term "eutectic point" is more general than "cryohydric point," the latter term being usually restricted to aqueous solutions. "Eutectic mixture" and "cryohydric mixture" ("cryohydrate") are similarly related.

If more than one compound is formed between A and B, each one will cause a *maximum point* in the curve, i.e., *each maximum will correspond to a compound.* The following examples will serve to make this clear:

1. The system SO_3+H_2O. Here there are a number of hydrates, which are indicated by the melting-point curve (Fig. 60).

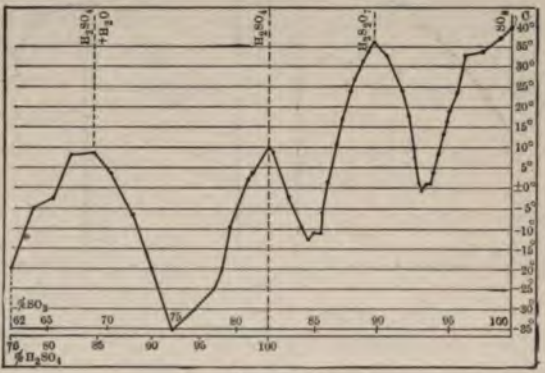


FIG. 60.

A mixture of 62% SO_3+38% H_2O has a freezing-point of −20°. On the addition of sulphur trioxide this point rises till at the composition $SO_3+2H_2O=H_2SO_4 \cdot H_2O$ it reaches its first maximum. At this temperature (8°) the whole mass solidifies, yielding crystals of the above composition. The further addition of sulphur trioxide has the same effect on the melting-point of the hydrate $H_2SO_4 \cdot H_2O$ as the ordinary addition of a foreign substance to a pure substance. At first the melting-point falls; that which crystallizes out is the hydrate $H_2SO_4 \cdot H_2O$. At a composition of about $3H_2O+2SO_3$ a eutectic point is reached (§ 237). The mass solidifies at −35° to a mixture of $H_2SO_4 \cdot H_2O$ and H_2SO_4. Continued addition of sulphur trioxide causes a rise of the melting-point till at +10° a second maximum is reached, where the whole solidifies to a homogeneous mass, consisting of pure sulphuric acid, H_2SO_4. Along this ascending branch of the curve H_2SO_4 crystallizes out. The melting-point curve then proceeds to a third maximum point, corresponding to the hydrate $H_2SO_4 + SO_3 = H_2S_2O_7$ (pyrosulphuric acid), and comes to an end in the melting-point of the asbestine form of sulphur trioxide at +40°.

2. In non-aqueous liquids the relations are almost exactly the same, as may be seen from a consideration of the system S+Cl. It was remarked in § 75 that, while the compound SCl_4 could not be isolated, the form of the melting-point curve left no doubt as to the existence of such a compound. This curve has a maximum at the point C_2 (Fig. 61), corresponding to 20 atomic per cent. sulphur, or to the molecular formula SCl_4. The points E_1, E_2, E_3 are the eutectic points for $S + S_2Cl_2$, $S_2Cl_2 + SCl_4$ and $SCl_4 + Cl_2$, respectively, while the maximum C_1 corresponds to the compound S_2Cl_2.

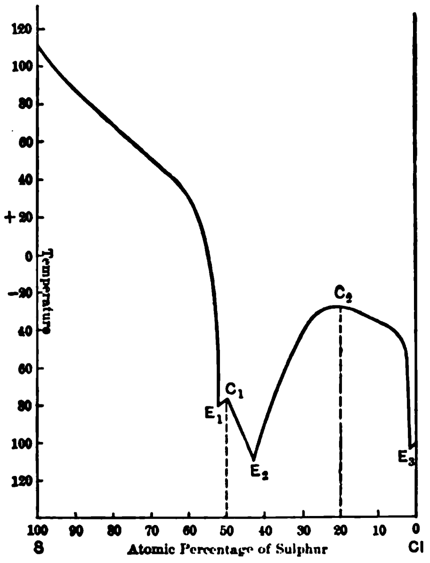


FIG. 61.

Supersaturated solutions.—A sodium sulphate solution saturated a little below 33° can, if carefully guarded from contact with any of the solid salt, be cooled down to room temperature without anything crystallizing out, but contact with the tiniest crystal fragment of $Na_2SO_4 \cdot 10H_2O$ is sufficient to cause a sudden crystallization of this salt.

Sodium sulphate is only one of a large number of salts capable of forming solutions of this nature. Sodium thiosulphate and many of the nitrates are other good examples. Such solutions are called *supersaturated*. They are perfectly stable; neither rubbing with a glass rod nor shaking (which treatment ordinarily tends to induce crystallization) causes the formation of crystals, provided no trace of the solid salt comes in contact with the solution. Such a system, which is *unstable under only one condition,* is called a **metastable system.**

If a supersaturated solution of sodium sulphate is cooled down below room temperature, another hydrate crystallizes out, viz., $Na_2SO_4 \cdot 7H_2O$; the resulting system is still metastable, however, for contact with the slightest trace of $Na_2SO_4 \cdot 10H_2O$ suffices to convert it entirely into the stable system, with the deposition of $Na_2SO_4 \cdot 10H_2O$.

The smallest amount of salt (crystal nucleus) that is sufficient to disturb and thus cause the disappearance of a metastable system, such as is represented by a supersaturated solution, is a quantity of about the order 10^{-10} g., according to OSTWALD. The extreme minuteness of this amount explains why a spontaneous disappearance of the metastable condition was formerly regarded as possible. Inasmuch as very small bits of crystals are always floating in the air (especially in laboratories), it is usually only necessary to open a bottle containing a supersaturated solution or to rub the sides with a glass rod (which always has crystal fragments on its surface), in order to excite crystallization into the stable system.

238. For the reasons stated in §§ 65 and 66 it is assumed that acids, bases and salts in aqueous solution are split up into ions. This dissociation can be more or less complete, according to the nature of the solute, the temperature of the solution and its concentration. Examples of this have already been mentioned here and there in the text; hydrochloric and nitric acids in tenth-normal solutions are almost completely dissociated, carbonic and silicic acids scarcely at all. Among the bases the hydroxides of potassium, sodium and the alkaline earth metals are almost completely dissociated at this dilution. A similar difference is shown by salts; those of the alkalies are practically completely ionized, while mercuric chloride is very slightly so. We shall return to this subject more in detail in the discussion of the metals.

The principle that solutions containing equivalent amounts of different electrolytes differ greatly in conductivity and hence in degree of ionization can be demonstrated in an elegant manner with the aid of an apparatus devised by WHITNEY (Fig. 62).

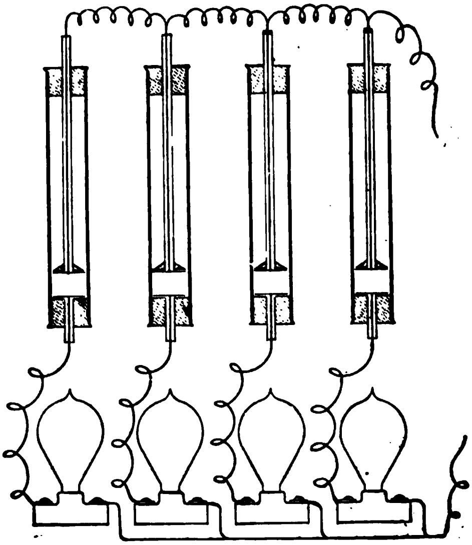


FIG. 62.

Four glass cylinders (3 cm. diam.) are fitted each with two horizontal platinum disks (copper can be used but is less satisfactory) to serve as electrodes, the upper ones being movable. Each lower electrode is connected with an incandescent lamp and the apparatus as a whole with the terminals of a (preferably) alternating 110-volt circuit. After placing in each of the tubes 120 cc. distilled water they are filled with 5 cc. of half-equivalent-normal hydrochloric, sulphuric, monochloracetic and acetic acids respectively. On making the distance between the electrodes alike in all the cylinders, the lamp beneath the hydrochloric acid is found to glow brightest, since the resistance of this solution is the least. The other lamps follow in brightness in the order given above. The electrodes are next adjusted so that all the lamps are equally bright, when it is seen that while the electrodes in the hydrochloric acid are farthest apart, those in the acetic acid are almost in contact.

In order to show that the alkali salts of these acids, unlike the acids themselves, have nearly the same conductivities and degrees of dissociation the solutions are just neutralized with potassium hydroxide and the lamp test repeated. The lamps are equally brilliant when the electrodes are at approximately the same height.

239. In the solution of an extensively ionized salt we should expect to find the properties of the cation and the anion. It must exhibit the sum of the properties of the two ions, or, to use other words, its properties must be **additive** with reference to those of both ions. This is actually the case, both physically and chemically. As for the chemical properties, we observe that solutions of different salts of the same metal all give the same reactions; from the solutions of all lead salts, for instance, hydrogen sulphide precipitates black lead sulphide, sulphuric acid white lead sulphate, etc. Similarly the solutions of salts of the same acid are all characterized by the same reactions; sulphates, for example, by the precipitate they give with barium chloride solution. All this appears very strange when we recall that the solid salts are markedly different from each other in their properties, but we are forced to just such a conclusion when we assume that the salts are ionized in solution.

Among the physical properties additivity is very apparent in the color of salts of colored acids and bases. OSTWALD found that all permanganates with a colorless base, when prepared in equivalent solutions, give exactly the same absorption spectrum (§ 263). All dilute copper solutions are blue. In the permanganates it is the anion MnO_4', in the copper solutions the cation $Cu^{\cdot\cdot}$, which is to be regarded as the color-carrier.

When the solvent is one in which ionization does not occur, the salts of the same base may differ widely in color. For instance, a solution of cobalt nitrate in alcohol is purple, that of the chloride is bluish violet; but if both are poured into an excess of water, the solution becomes pink in each case. Another example is found in the alcoholic solutions of cupric chloride and nitrate; the former is dark green, the latter blue; on the addition of water both become blue.

This additive nature manifests itself in various other physical properties also. But since it cannot usually be shown directly (as in the case of colored salts), we have to approach the matter somewhat indirectly, as the following example will illustrate. The specific gravity of a sugar solution can be represented fairly accurately by the formula

$$S=1+K\cdot n,$$

n being the number of moles per liter and K a constant. Similarly in the case of the solution of a highly ionized salt whose specific gravity is raised to $1+\alpha n$ by the anion, to $1+\beta n$ by the cation, α and β being constants, the specific gravity of the solution, if we assume additivity to exist, must be

$$S=1+n(\alpha+\beta).$$

The values of α and β are as yet unknown. For salts with the same anion the specific gravity is expressed by

$$S_1=1+n(\alpha+\beta_1);\quad S_2=1+n(\alpha+\beta_2);\quad S_3=1+n(\alpha+\beta_3),\ \text{etc.}$$

For salts with the same anions as in the former case but with a different cation the specific gravities of their solutions are represented thus:

$$S_1'=1+n(\alpha_1+\beta_1);\quad S_2'=1+n(\alpha_1+\beta_2);\quad S_3'=1+n(\alpha_1+\beta_3),\ \text{etc.,}$$

whence it follows that the differences S_1-S_1', S_2-S_2', S_3-S_3', $=n(\alpha-\alpha_1)$, must always have the same value in case additivity really exists. The equality of these differences can therefore be used as a proof of additivity.

A concrete example of the above reasoning is to be found in the specific gravity values of the solutions KCl, NaCl, NH_4Cl and KBr, NaBr, NH_4Br. Here we actually have the relationship:

$$\mathrm{KCl-KBr=NaCl-NaBr=NH_4Cl-NH_4Br;}$$

however, not simply in specific gravity but with reference to other physical constants as well. Compressibility, capillarity and refractive index, for example, have been found to conform to this same additive scheme.

The ionization hypothesis also leads us to predict that when dilute solutions of strong acids and bases, each containing one mole, are mixed, the same caloric effect will be observed. This is found to be the case (13.8 cal.). The only change that takes place in the mixing is the formation of water from its ions (§ 66). Further, the so-called **law of thermo-neutrality,** which says that when two dilute salt solutions are mixed there is no caloric effect, is a natural consequence; for the ions of the two salts exist in the free state both before and after the mixing.

ACIDIMETRY AND ALKALIMETRY. THEORY OF INDICATORS.

240. The amount of acid or base present in a liquid can be determined most simply by volumetric analysis (§ 93). Those parts of volumetric analysis which comprise the methods used for this purpose are known as *acidimetry* and *alkalimetry*. Suppose that we wish to determine the amount of hydrochloric acid present in a given volume of liquid. A known volume of this liquid (50 cc., 10 cc., or less, according to the supposed concentration) is measured out and sodium hydroxide solution of known concentration is slowly added from a burette. When the point has been found at which the liquid becomes neutral, it is easy to calculate the concentration of the acid from the number of cubic centimeters of sodium hydroxide consumed.

Example. Determine the amount of nitric acid present in a liter of a solution of this acid if 10 cc. are neutralized by 7.3 cc. of a normal alkali solution. These 7.3 cc. are equivalent to the same number of cubic centimeters of normal nitric acid. Therefore the 10 cc. contain 7.3 milligram molecules of nitric acid or 63×7.3 mg. One liter must contain a hundred times as much, or 45.99 g.

Before we can determine the concentration of an acid or an alkali in this manner, we must first possess an alkali or base solution of known concentration and further have a delicate means of detecting when the liquid is exactly neutralized.

1. *Preparation of an acid and an alkali of known concentration.* This can be done in various ways. Oxalic acid, $C_2H_2O_4 \cdot 2H_2O$, succinic acid, $C_4H_6O_4$, or tartaric acid, $C_4H_6O_6$, can be used as the basis, for all of these are crystallized solids and can be easily obtained in a state of sufficient purity; hence the amount of acid dissolved

can be very accurately determined by previously weighing the substance on an analytical balance. We thus weigh out 1 g.-equivalent ($\frac{1}{2}$ g.-mol.) of one of these acids, dissolve it in water and dilute to exactly a liter. Thereupon with the help of this normal acid a normal alkali is prepared; a little more than 1 or $\frac{1}{2}$ or $\frac{1}{10}$, etc., gram-equivalent of sodium hydroxide or potassium hydroxide (barium hydroxide is also very satisfactory) is dissolved in water and this solution is standardized according to the normal acid, i.e the concentration is determined by titration with normal acid and then diluted so that it is just normal.

Sodium carbonate can also be used as a basis. After being first heated in order to expel all moisture it is weighed out and dissolved in water. This solution is heated to boiling and covered with a glass plate with a hole in it, through which the nozzle of a burette is passed. The solution of the acid whose concentration is to be determined is then allowed to flow from the burette into the boiling liquid till neutralization is effected. Carbon dioxide escapes, but the glass plate prevents any loss of the liquid by spurting.

The standardizing can also be accomplished by adding the acid solution that is to be standardized to a mixed solution of potassium iodide and potassium iodate. Hydriodic and iodic acids are set free and they react at once in the following manner:

$$5KI + KIO_3 + 6HX = 5HI + HIO_3 + 6KX; \quad 5HI + HIO_3 = 3H_2O + 6I.$$

Thus for every equivalent of acid one atom of iodine is set free. By titrating with sodium thiosulphate the amount of iodine liberated can be determined. This method gives very accurate results.

2. *Determination of the point at which the liquid becomes neutral.* Since the point of neutralization of an acid by a base or *vice versa*, is not indicated by any visible phenomena, a minute quantity of some substance is added whose color is altered by an excess of the neutralizing liquid. Such substances are *litmus* (blue in alkaline and red in acid solutions), *phenolphthaleïn* (red in alkaline, colorless in acid solutions), *methyl orange* (yellow in alkaline, red in acid solutions), and many others. Therefore, on gradually adding an $\frac{\text{alkaline}}{\text{acid}}$ solution to an $\frac{\text{acid}}{\text{alkaline}}$ solution in the presence of one of

these substances a *change of color* will be noticed when the point of neutrality is just passed. Coloring-matters like the above are termed **indicators.** The change of color is due in many cases to a transformation of the substance into a salt whose free acid is very unstable and passes over almost immediately into an isomer having a different color from the free acid or the salt.

241. From the standpoint of the ionic theory the following **theory of indicators** has been advanced: If a couple of drops of the indicator are introduced into an acid solution, the ionization of the indicator, which is only very slight, is reduced by the great excess of acid to practically zero. If a base is then added, the H-ions of the acid to be titrated are removed by the OH-ions. However, if the acid is very strong, enough H-ions remain in the liquid up to the last to prevent anything like an extensive ionization of the coloring-substance; not until the first excessive drop of alkali is added do the anions of the coloring-substance come into existence, the alkali compound of the latter being strongly dissociated. *The change of color is therefore sharply defined,* for it is due to this difference in color of the non-ionized molecule and the anion. On the other hand, if the acid is a weak one, there will not be enough H-ions present when the end of the titration is nearly reached to prevent a slight ionization of the coloring-substance. As a result we shall have in the solution not only the undissociated coloring-substance but its anions as well, even before the titration is completed,—in other words, *the change of color becomes more gradual* and hence the end reaction more indefinite. The effect will be the same if the alkali employed contains carbonate. In that case near the end of the titration the solution will only contain carbonic acid, which is very weak; consequently the color change will not be sudden. It is for this reason that in titrating soda solutions (see § 240) the carbonic acid must be expelled by boiling.

If a weak acid is to be titrated, it is necessary, according to the above, to select an indicator which is much less ionized even than the acid itself and whose alkali salts are sufficiently ionized to produce a distinct change of color. A very suitable one for this purpose is phenolphthaleïn. Acetic acid, for example, can be satisfactorily titrated with it, if a strong base is employed, for the reasons set forth above. On the other hand, in case a weak base is to be titrated, phenolphthaleïn is not so satisfactory. Ammonia does not color a phenolphthaleïn solution till a considerable excess is added, because at the great dilution in which the ammonium-phenolphthaleïn compound exists in a titration it is almost completely split up by hydrolysis (§ 66).

If a weak base is to be titrated, an indicator must be selected which is a relatively strong acid, for then the salt of the coloring-substance will be hydrolyzed only to a limited extent, even near the termination of the titration (i.e. when the concentration of the base has become weak), and the color of its ions will therefore still predominate. For such a titration a strong acid (e.g. hydrochloric or sulphuric acid) must be used, in order that the first drop after the point of neutralization is reached may diminish the electrolytic dissociation of the coloring-substance and so give the solution the color of the non-ionized molecules. *Methyl orange* is an indicator that answers these requirements; it serves very well in the titration of ammonia. All other indicators are intermediate to these two extremes (phenolphthaleïn and methyl orange) as regards their ionization, and their applicability is determined accordingly.

COPPER.

242. This metal occurs *native* in America, China and Japan, forming regular crystals. Other copper minerals are *cuprite* (Cu_2O), *malachite* and *azurite* (both basic carbonates), *chalcocite* (Cu_2S) and particularly *chalcopyrite*, or *copper pyrites* ($CuFeS_2$). The United States furnishes about 60% of the world's copper supply.

The extraction of the metal from non-sulphurous ores is very simple. They are smelted with coal and thus reduced to the metallic state. If the copper ore contains sulphur, the metallurgical process is much more complicated and has numerous modifications. The ore is broken up and "calcined" so as to convert some of the copper sulphide into copper oxide. Thereupon it is fused with sand and other siliceous fluxes (as well as coal for reducing copper sulphate), and the iron, but not the copper, is converted into silicate. The object of the flux, here as with other metals, is to lower the fusing temperature of the ore and collect the impurities (iron in this case) into a "slag" consisting of fused silicates, etc. The slag floats and can be run off. The fusion process is repeated until all the iron is eliminated. The resulting mixture of impure copper sulphide and copper oxide is called *matte* (also *regulus* and *coarse metal*). By repeated roasting and fusing, crude metallic copper is obtained:

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

Finally it is fused with coal to reduce any copper oxide remaining.

Refining. The copper thus obtained often contains small quantities of other metals. Since these impurities lower its conductivity, a better grade is demanded for electrical purposes. Crude copper is now refined by an *electrolytic process* which yields chemically pure copper. If an impure copper solution is electrolyzed, it is possible under suitable conditions to precipitate pure copper in a compact mass, while the impurities remain in solution or are deposited as powder. From this powder ("slimes") a considerable amount of gold and silver is obtained.

The usual arrangement is to suspend plates ("anodes") of crude copper and thin sheets of pure copper alternately in a copper vitriol solution acidified with sulphuric acid. If the crude plates are then connected with the positive pole and the thin sheets with the negative pole of the dynamo current, pure copper is deposited on the sheets, while an equivalent amount of the crude copper dissolves to take its place.

Physical Properties. Copper has a bright red color. It is rather hard but very extensible and flexible; it can be drawn out into very fine wire and beaten into extremely thin sheets (imitation gold-leaf), which are green in transmitted light. Sp. g. = 8.94; melting-point = 1045°.

Chemical Properties. In dry air copper is permanent at ordinary temperatures, but in moist air it becomes covered with a thin coating of basic copper carbonate, which protects it from further rusting. On being heated in the air it turns to copper oxide, CuO. It is readily attacked by nitric acid (§ 120), but not by dilute hydrochloric acid. Sulphuric acid has no effect on it at ordinary temperatures, but at higher temperatures a reaction takes place in which sulphur dioxide is given off (§ 78). Ammonia and oxygen dissolve it to form a blue liquid, copper oxide ammonia. Copper is deposited from solutions of its salts by iron, magnesium and other metals.

Uses and alloys. Copper finds extensive use in the arts, both as such and in alloys. The well-known yellow brass is an alloy of 1 part zinc and 2 parts copper and is harder than copper itself. German silver consists of about 50% Cu, 25% Ni, and 25% Zn; its electrical conductivity is affected very little by changes of temperature, which makes it valuable for resistance coils, etc. For bronzes see § 199.

Copper is employed in large quantities in electrotyping. A cast is first constructed of plaster of Paris and made a conductor by being coated with graphite, whereupon it is suspended by the wire of a battery into a copper sulphate solution; a plate of pure copper serves as the anode. If the potential difference at the electrodes is properly regulated, the copper is deposited on the plaster cast in compact form, so that all the details of the original are reproduced with the greatest fidelity.

Compounds of Copper.

243. Copper forms two sets of salts, which are derived from the oxides Cu_2O, *cuprous oxide*, and CuO, *cupric oxide*.

CUPROUS COMPOUNDS.

Cuprous oxide, Cu_2O, can be obtained from cupric salts in various ways, e.g. by reducing them in alkaline solution with grape sugar, hydroxylamine, arsenious acid, or the like. It forms a reddish-yellow crystalline powder, which is unaffected by the air at ordinary temperatures. It dissolves in ammonia; this solution rapidly turns blue because of the absorption of oxygen, the cuprous oxide going over into cupric oxide. Cuprous oxide is transformed by sulphuric acid into copper sulphate and copper:

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

It is possible that cuprous sulphate is first formed and that the cuprous ions of this solution are forthwith changed into cupric ions and non-ionized copper, $2Cu^{\cdot} = Cu^{\cdot\cdot} + Cu$.

Of the **cuprous salts** only those of the halogens are known. Cu_2Cl_2, Cu_2Br_2 and Cu_2I_2 are all "insoluble" (*cf.* § 235); their solubility decreases with increasing atomic weight of the halogen.

Cuprous chloride, Cu_2Cl_2 (the vapor density indicates this doubled formula), separates out when a solution of cupric chloride is boiled with copper, or when a mixed solution of copper sulphate and sodium chloride is saturated with sulphur dioxide gas and the resulting liquid poured into water. It is a white crystalline substance, which must be kept under water, for it absorbs oxygen rapidly when moist and turns green because of the formation of basic copper chloride, $CuCl \cdot OH$. It melts at 430° and distils at about 1000°. It is soluble in concentrated hydrochloric acid and in ammonia. These solutions are at first colorless but very soon become blue because of the absorption of oxygen (formation of cupric compounds). They also have the power of absorbing carbon monoxide, forming an unstable compound, $Cu_2Cl_2 \cdot CO \cdot 2H_2O$, which crystallizes in colorless laminæ. Use is made of this property in gas analysis.

Cuprous iodide, Cu_2I_2, is formed when a solution of copper sulphate is treated with potassium iodide, half of the iodine being liberated:

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2.$$

It may be supposed that cupric iodide is first formed and that it then breaks up into cuprous iodide and iodine, or, rather, that the ions of cupric iodide interact thus:

$$Cu^{\cdot\cdot} + 2I' = CuI + I,$$

the cuprous iodide being unionized because "insoluble."

According to Ostwald, however, an equilibrium is formed here, for, though the cuprous iodide is but slightly soluble, the reaction does not complete itself and some cupric ions still remain in solution. The reversibility of this reaction is evident from the fact that cuprous iodide is dissolved by an alcoholic iodine solution, so that we have

$$Cu^{\cdot\cdot} + 2I' \rightleftarrows CuI + I.$$

Therefore, in order to make the precipitation more complete, a substance (SO_2) is added, which will remove the iodine, one of the reaction products. This treatment is especially effective because the iodine is thereby converted into ions and this raises the concentration of one of the components on the left side of the equilibrium equation.

Cuprous cyanide, $Cu_2(CN)_2$, can be obtained in a manner analogous to that described for cuprous iodide, viz., by mixing solutions of copper sulphate and potassium cyanide. Half of the cyanogen escapes as gas:

$$2CuSO_4 + 4KCN = 2K_2SO_4 + Cu_2(CN)_2 + (CN)_2.$$

Cuprous cyanide dissolves very rapidly in an excess of potassium cyanide, forming a salt, $2KCN \cdot Cu_2(CN)_2$, which contains a complex anion $[Cu_2(CN)_4]''$. Practically all of the copper ions go to form these complex ions on the addition of potassium cyanide, for the solution gives none of the ordinary reactions for copper, not even that with hydrogen sulphide, although copper sulphide is precipitated by this reagent even when the concentration of the copper ions is very slight (§ 73).

CUPRIC COMPOUNDS.

244. Cupric oxide, CuO, is a dense, black powder, obtained by heating copper in the presence of oxygen at a high temperature. It can also be prepared by heating the nitrate to redness or igniting the hydroxide or the carbonate. When finely divided it occludes on its surface large amounts of steam. It finds extensive use in organic analysis.

Cupric hydroxide, $CuO \cdot nH_2O$, separates out as a flocculent, voluminous blue precipitate (hydrogel, § 195) when the solution of a copper salt is treated with caustic potash or soda. On boiling the liquid it turns black, water being liberated and cupric oxide formed.

Cupric chloride, $CuCl_2 \cdot 2H_2O$, is obtained by dissolving cupric oxide or carbonate in hydrochloric acid. It crystallizes in blue rhombic needles, which, however, often appear green because of mother-liquor adhering to them. It is readily soluble in water and alcohol. The anhydrous salt is yellow; the concentrated aqueous solution is green; the dilute solution is blue. This difference can be attributed to the breaking up of the salt into its ions, for all dilute copper solutions are blue, no matter what the acid radical is. It therefore follows that the copper ion imparts a blue color to solutions. In a concentrated solution of cupric chloride the yellow color of the undissociated molecules forms with the blue of the copper ions a green color.

The following phenomenon is rather peculiar. If water is added to a solution of cupric chloride till it is just blue and the liquid is then warmed, the color changes to green. According to the above explanation of the change of color the electrolytic dissociation must diminish on warming, wherefore, in accordance with the principle of mobile equilibrium (§ 235), the heat of ionization must be positive, or, in other words, heat must be evolved when the salt splits up into its ions. Experiments by ARRHENIUS have shown this to be true for certain salts, e.g. copper sulphate, so that it may also be assumed here.

On mixing a copper sulphate solution with a concentrated sodium chloride solution the color turns green because of the formation of $CuCl_2$ molecules. We should therefore expect this same result when an excess of chlorine ions is introduced into any copper solution, and experience has shown this to be the case.

Cupric bromide is analogous to the chloride; **cupric iodide** is unstable, decomposing at once into iodine and cuprous iodide (§ 243).

Copper sulphate, $CuSO_4 \cdot 5H_2O$, blue vitriol, is the most familiar salt of copper. It is obtained as a by-product, chiefly from gold and silver refineries, and is also manufactured by dissolving copper in sulphuric acid. It crystallizes in large blue triclinic crystals, which lose four molecules of water at 100°; the fifth is liberated at 200°. The anhydrous copper sulphate is a white powder, which absorbs water greedily, turning blue again. At 20° 100 parts H_2O dissolve 42.31 parts of the crystallized sulphate. Blue vitriol is employed in large quantities in electroplating, etc. (§ 242).

Copper nitrate, $Cu(NO_3)_2$, can crystallize with three or six molecules of water and is dark blue.

Copper carbonate. The normal salt is unknown, but basic salts have been prepared.

Copper arsenite, $CuHAsO_3$, is used as a pigment under the name of *Scheele's* green. *Schweinfurth green,* or *Paris green,* is a double compound of copper arsenite and copper acetate. Since both are very poisonous, their use in dyeing textile fabrics, wall-paper, etc. (§ 157) is being restricted.

Copper sulphide, CuS, is formed as a black precipitate by passing hydrogen sulphide into a copper solution. When moist it oxidizes slowly in the air to copper sulphate. On being heated in a current of hydrogen it yields cuprous sulphide, Cu_2S, and hydrogen sulphide.

Copper salts and ammonia. On mixing a solution of ammonia with a copper salt, a precipitate of copper hydroxide is first formed, if not too much ammonia is used; this precipitate is dissolved by an excess of ammonia to a dark blue solution. If the latter is evaporated or treated with alcohol, ammoniacal compounds crystallize out; a typical one is $CuSO_4 \cdot 4NH_3 \cdot H_2O$, which is transformed into $CuSO_4 \cdot 2NH_3$ on being heated to 150°. The aqueous solutions of these substances are to be assumed to contain complex ions of copper and ammonia, since they do not give some of the ordinary copper reactions, e.g. precipitation with caustic potash. The fact that certain other reactions of copper do however appear, e.g. precipitation with hydrogen sulphide, proves that free copper ions are still present in the liquid, although only to a small extent.

SILVER.

245. This metal occurs *native;* nuggets weighing 100 kilos are not unknown. The important silver ores are *argentite,* Ag_2S, *stromeyerite,* $Cu_2S \cdot Ag_2S$, *pyrargyrite,* $3Ag_2S \cdot Sb_2S_3$, and *stephanite,* Ag_5S_4Sb. It is also found in smaller amounts in *cerargyrite,* or *horn silver,* $AgCl$. Traces of silver compounds are known to exist in sea-water. Many lead ores, e.g. galenite, contain a small percentage of silver and in some cases it is extracted.

The chief silver-producing countries are the United States (Colorado and neighboring States), Mexico, Australia and Bolivia. The present annual world's production of silver is about 54,000,000 fine ounces (1,680,000 kg.).

The *metallurgy* of silver is rather complicated; several processes are employed.

(1) The sulphurous ores are roasted in the air, whereby the sulphate, Ag_2SO_4, is formed. This is extracted with water and the silver precipitated from the solution by iron.

(2) The ores containing free silver are roasted with common salt, thus yielding silver chloride. The latter is then brought into solution by means of sodium thiosulphate and sodium sulphide is added to precipitate the sulphide of silver. This is then converted into the metal by heating at a high temperature.

(3) Amalgamation Process. In Mexico, where there is lack of fuel, the ores, finely powdered, are stirred into water and treated with sodium chloride; this mud is intimately mixed by spreading it out on a floor (*Patio*) and driving mules through it. Thereupon some mercury is added, as well as a mixture of ferric and cupric salts, and the whole is worked over thoroughly for several days. The liberated silver forms an amalgam with the mercury and can be obtained by distilling off the mercury. In the above process the following reactions probably take place:

$$2CuCl_2 + Ag_2S = Cu_2Cl_2 + 2AgCl + S.$$

The cuprous chloride, Cu_2Cl_2, dissolves in the brine and reacts with another portion of silver sulphide:

$$Cu_2Cl_2 + Ag_2S = Cu_2S + 2AgCl.$$

The silver chloride dissolves in the brine and the silver is precipitated from solution by mercury, which goes over into calomel.

(4) Lead ores usually contain some silver. In the smelting of lead the silver all goes into the lead and is recovered from it in the following way: The argentiferous lead is fused and then cooled slowly till it begins to congeal. Just as pure ice crystallizes out of a dilute salt solution on cooling, so the lead separates out here in crystals free from silver. These are removed and this process—called *Pattinsonizing* after its inventor—is kept up till the percentage of silver reaches about 1%. This rich lead is then subjected to the cupellation process, i.e. the lead is fused in a reverberatory furnace, whose hearth consists of a porous mass (cupel, or test). The lead is oxidized to the easily fusible oxide PbO (litharge) which is partly driven off by a blast from time to time through the channel provided for its escape, and partly absorbed by the porous material (bone-ash, or clay and limestone) of the cupel. Towards the end of the process the film of litharge remaining becomes so thin that the silver beneath reflects the light, producing a beautiful iridescence. Here and there the film breaks, disclosing the brilliant surface of the metal (" brightening " of the silver). The silver is finally left in the metallic state.

Another method (PARKES') is based on the facts that silver dissolves very readily in molten zinc and zinc only slightly in molten lead. The fused lead can therefore be extracted with fused zinc (*cf.* ORG. CHEM., § 24). The process is as follows: To the fused argentiferous lead some zinc (containing 0.5% Al) is added and the mixture is stirred. The zinc takes up most of the silver from the lead and floats on the molten mass. It is skimmed off and cast into plates, which serve as the anodes in the subsequent electrolysis. At the cathode nearly pure zinc is deposited, while silver powder (70–80% Ag, the rest Pb) sinks to the bottom and is removed to the cupel.

The electrolytic refining of silver is now carried on extensively in America. A great deal is recovered from the copper slimes (§ 242).

The pure silver of commerce usually contains a little copper and other metals; STAS obtained it chemically pure by dissolving the product of the smelter in nitric acid and precipitating it with hydrochloric acid as the chloride; this was then reduced by boiling with dilute caustic potash and milk sugar and finally distilled with the aid of an oxyhydrogen flame in an apparatus made of lime.

Physical Properties. Silver crystallizes in regular octahedrons. It has a white color and a high lustre. It is the best conductor of heat and electricity of all the metals and it is very malleable and ductile. Sp. g. = 10.5; m.-pt. = 954°. At an elevated temperature it volatilizes in the form of a blue vapor (STAS). Molten silver absorbs oxygen, but allows it to escape on becoming solid (§ 9).

Chemical Properties. Silver is one of the precious metals; this term is applied chemically to those metals which do not combine with oxygen directly (under ordinary pressure) either at ordinary or higher temperatures. If, however, the pressure is raised, silver combines with oxygen directly at an elevated temperature:

$$2Ag + O \rightleftarrows Ag_2O.$$

Nitric acid attacks it readily at ordinary temperatures, sulphuric acid only at higher temperatures; hydrochloric acid has very little effect on it.

Uses; alloys. Pure silver is seldom made use of practically, but its alloys are employed in the manufacture of silverware and coins. For these purposes an alloy with copper is used. Silver plate and jewelry usually contain 75 or more per cent of silver; the silver coins of the United States and continental countries consist of 90% silver and 10% copper; the English shillings ("sterling" silver) contain 92.5% silver. The admixture of copper makes the metal harder.

Considerable silver is consumed in silvering objects of copper or other metals (silver-plating). At present this is usually done by electrolysis (§ 242). The object to be plated is made the cathode and a silver plate the anode; the bath consists of silver cyanide dissolved in an excess of potassium cyanide.

Compounds of Silver.

246. The known oxides are: Ag_4O, *silver suboxide* (very unstable); Ag_2O, *silver oxide*, from which the salts of silver can be derived; and AgO, *silver peroxide* (formed from silver and ozone).

Silver oxide, Ag_2O, is deposited as a dark brown amorphous precipitate when the solution of a silver salt is treated with caustic soda or baryta-water free from carbonic acid. It is somewhat soluble in water (2.16×10^{-4} mole per liter at 25°); the solution probably contains the *silver hydroxide*, for it reacts alkaline and must therefore contain hydroxyl ions. In its saturated aqueous solution 70% of the molecules are found to be ionized. Silver hydroxide is thus not so strong a base as the alkalies, but considerably stronger than ammonia. Moist silver oxide (AgOH) absorbs carbon dioxide from the air and the silver salts react neutral, while the salts of most of the other heavy metals give an acid reaction because of a slight hydrolytic dissociation in aqueous solution. By heating to 250° silver oxide is broken up into its elements. It is reduced by hydrogen at as low a temperature at 100°. Ammonia water dissolves it readily because of the formation of a complex ion, $Ag(NH_3)_2^{\cdot}$.

Silver chloride, AgCl, is obtained by precipitating a silver solution with hydrochloric acid or a soluble chloride like sodium chloride; it forms a characteristic "curdy" precipitate. It is almost insoluble in water, 1 part in 715,800 H_2O at 13.8°.

When a silver solution is added very carefully to a sodium chloride solution (or to another chloride), a point can be found when the liquid gives a cloudiness (due to AgCl) with either solution. This must be attributed to the fact that the liquid is saturated with silver chloride and contains no other silver salt nor any other chloride. In view of the very high dilution of such a silver chloride solution (see above) it may be assumed that the dissolved part is completely ionized. If silver or chlorine ions are now introduced into the liquid, the ionization of the silver chloride is diminished and AgCl molecules are formed, but these cannot remain in solution, since the solution is already saturated with them.

Silver chloride dissolves readily in ammonia, potassium cyanide and sodium thiosulphate, forming complex ions.

If a solution of silver chloride and ammonia is allowed to evaporate in the dark at room temperature, silver chloride crystallizes out in finely developed octahedrons.

Silver bromide, AgBr, is less soluble than the chloride and has a yellowish color. It dissolves with difficulty in ammonia but easily in thiosulphate. **Silver iodide,** AgI, is even less soluble than silver bromide at ordinary temperatures. It is insoluble in ammonia. It is yellow. At high temperatures these halides melt and on cooling form a horny mass, which can be cut with the knife ("horn-silver," *cf.* § 245). **Silver fluoride,** AgF, is much more soluble in water than the three preceding halogen compounds.

Potassium silver cyanide, $KAg(CN)_2$, obtained on adding potassium cyanide to a silver solution, dissolves readily in water and is used in large quantities in electro-plating. When a current passes through it, potassium is deposited (primarily) at the cathode, while the anion $Ag(CN)_2'$ wanders to the anode; however, potassium precipitates silver from potassium silver cyanide:

$$K + KAg(CN)_2 = 2KCN + Ag.$$

Thus silver is deposited on the cathode while the anion $Ag(CN)_2'$ takes up an atom of silver at the silver anode to form silver cyanide and again unites with potassium cyanide to form the double salt; if the anode is of platinum, cyanogen gas is set free from the anion $Ag(CN)_2'$, and the anode becomes covered with silver cyanide, which soon interrupts the current.

All the silver salts, particularly the chloride, bromide and iodide, are sensitive to light, i.e. they are decomposed by light, especially by the violet and ultra-violet rays of the spectrum; as a result, the halogen passes off and the color of the salt becomes first violet and then black. A blackened preparation of this sort can be re-whitened by chlorine-or bromine-water. The sensitiveness to light depends in large measure on the manner in which the silver halide is precipitated.

247. *Photography.* The property of silver chloride and silver bromide just mentioned forms the basis of photography. The process is essentially as follows: A glass plate is coated with a "sensitive film," i.e. a thin layer of silver chloride or bromide is spread over it. Formerly this was usually prepared by the photographers themselves from collodion (see ORG. CHEM., § 231) which contained a halogen salt, e.g. CdI_2, in solution. After the evaporation of the solvent a halide coating remained, and by dipping the plates so prepared into a solution of silver nitrate, the silver halide was formed on them. These were the "wet plates"; now they are almost entirely superseded by the "dry plates."

The latter are prepared commercially on a large scale. They consist of a film of silver bromide in gelatine (less frequently in collodion) on a glass plate.

A sensitive plate of this sort is placed in the photographic apparatus, which is essentially a *camera obscura*, and the plate is there "exposed" to a light-image, which affects the silver halide chemically. It is very probable that by the action of the light a subhalide is formed; the liberated bromine enters into combination with the gelatine or the collodion and is therefore unable to transform the subhalide into halide. As yet no picture can be seen on the plate; it must first be "developed." For the latter purpose the plate is immersed in a liquid containing a reducing substance. A typical developer is a solution of ferrous oxalate in an excess of potassium oxalate; various other organic compounds (amidophenols, etc.) are at present frequently used. At those places on the plate where the light has struck, more or less silver (according to the intensity of the action of the light) is set free in the metallic form as a very thin coating, while the remaining silver halide is not affected by the developer. This halide must next be removed, else it would be decomposed by the light and more silver liberated; therefore it is immersed in a solution of sodium thiosulphate ("hypo"). This operation is called "fixing" the image. Up to this time the plate must be kept from the light.

After the fixing we have a so-called negative, i. e. there remains on the glass plate a picture which is black in those places which were illuminated in the object and clear on those places which were dark. From this a positive impression is prepared by laying the negative on a paper coated with a sensitive film and exposing the whole to direct sunlight. Those places on the negative where silver was deposited let no light or very little through (according to their thickness), so that a positive image is now produced. Finally the positive image is also fixed, for which purpose a bath containing thiosulphate and a little gold chloride is used. The latter improves the color-tone of the photograph.

The photographic process in its various stages is very interesting also from a theoretical standpoint and deserves a little more detailed study.

1. Preparation of the Plates.—A mixture is made of solutions of silver nitrate and ammonium bromide containing enough gelatine to make them congeal at room temperature. No separation of silver bromide is observed immediately on mixing, as is the case when the corresponding aqueous solutions are mixed. It may be assumed that the gelatine acts as a protective colloid toward the silver bromide, which of itself is unable to form a hydrosol (cf. § 196). That silver bromide is really formed can be demonstrated by measuring the electrical conductivity. If, instead of the silver bromide, its ions, $Ag^{\cdot}$ and Br', were present, the conductance would have to be much greater than that corresponding to the ammonium nitrate which results from the mixing ($AgNO_3+NH_4Br=AgBr+NH_4NO_3$). The observed conductance is, however, very nearly equal to that of a gelatinous solution of ammonium nitrate having the same concentration. This freshly prepared colloidal silver bromide in gelatine is relatively not very sensitive to light. In order to increase its sensitiveness the mixture is allowed to "ripen" by standing in the warm for a considerable length of time. It then loses its transparency and becomes yellowish white. The resulting increase in sensitiveness must be accounted for by supposing that the light is not sufficiently absorbed by the transparent colloidal silver bromide to exert its full action, and that this is only accomplished when in the process of ripening the colloid is slowly coagulated, the finer particles of silver bromide having collected to form larger ones, which render the mass opaque and therefore increase its absorptive power. The ripened silver bromide gelatine is then spread upon the plates.

2. The Latent Image.—When the plates are exposed to light there is formed upon them silver subbromide, Ag_2Br,—not metallic silver, since treatment with dilute nitric acid does not destroy the latent image. Besides silver subbromide, free bromine is also formed during the expo-

sure; if a closed apparatus is used and it is afterward placed in the dark, silver bromide is formed again. Moreover not all the silver bromide is decomposed, but an equilibrium is established:

$$2AgBr \rightleftarrows Ag_2Br + Br,$$

which is displaced farther to the right, the stronger the illumination. Light thus plays the same role in this dissociation as heat in other dissociations. If a gelatine plate is used the latent image remains for months unaltered because the free bromine is taken up by the gelatine.

3. Developing.—This process is explained by some as follows: By the reducing action of the developer silver is immediately set free from silver subbromide but not from silver bromide, notwithstanding that the latter is capable of being reduced. The system silver bromide plus developer can be compared to a supersaturated solution, which only deposits solid salt when it comes in contact with a crystalline nucleus of salt (*cf.* § 237). The nuclei of metallic silver are furnished by the silver separated out of the subbromide. The deposition of additional silver molecules takes place only upon those molecules already there and not on spots where there was no subbromide originally, i.e. silver is deposited only where the light acted on the plate. According to this nucleus theory the developing process would be comparable to the following experiment: If a few letters are written on a glass plate with a piece of alum and the plate is laid in a supersaturated solution of this salt, the letters become visible, because alum is deposited on them.

Silver sulphate, Ag_2SO_4, is obtained by dissolving silver in hot concentrated sulphuric acid. It is scarcely soluble in cold water.

Silver nitrate, $AgNO_3$, prepared by dissolving silver in nitric acid, crystallizes isomorphous with saltpetre in beautiful rhombic crystals. It is very soluble in water (1 part in 0.5 part at room temperature) and melts at 218°. In medicine it is frequently employed, especially as a caustic; it goes under the name of "lunar caustic." Indelible inks are also prepared from it.

Silver nitrite, $AgNO_2$, is formed as a yellowish precipitate on mixing an aqueous alkali nitrite solution and silver nitrite; it dissolves in boiling water and crystallizes on cooling in beautiful needles.

GOLD.

248. This metal generally occurs *native*, being found in beds of quartz and alluvial deposits resulting from the decay of quartz rocks. Traces of gold have been detected in sea-water. It occurs in Hungary, Transylvania, the Ural and particularly in Australia, in Transvaal and in the western part of the United States and Canada. Recently large quantities have been discovered in Alaska (Klondike region). In Colorado considerable gold is obtained from tellurides (*sylvanite*, etc.).

Inasmuch as the amount of gold contained in a cubic meter of ore or rock in the most profitable instances is only very small, it becomes the task of metallurgy to extract it from proportionately large quantities of rock.

In the Transvaal this is accomplished as follows: The gold occurs there in so-called *reefs*, which are vertical veins in the quartz. These reefs are seldom more than one meter thick, but extend for miles east and west; their depth is unknown. They are mined by blasting with dynamite; the large pieces are reduced to about the size of an egg in a heavy iron apparatus and then sent to the stamps, that move in a large trough through which plenty of water is kept running. The water carries off the fine auriferous slime, which is made to flow over amalgamated copper plates that are somewhat inclined. The gold is retained by the mercury. After some time the plates are scraped off and the mercury removed by distillation, leaving the gold.

The extracted slime ("tailings") is treated again for gold, for which purpose the cyanide process of SIEMENS is employed.

By this process the tailings are allowed to stand for from one day to three weeks in contact with a 0.1 to 0.01% potassium cyanide solution. Under the influence of the oxygen of the air the gold dissolves in it, forming a double cyanide, $KAu(CN)_2$:

$$2Au + 4KCN + 2H_2O + O_2 = 2KAu(CN)_2 + 2KOH + H_2O_2.$$

Hydrogen peroxide is also formed and serves to bring further amounts of gold into solution:

$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH.$$

From this solution the gold is obtained by electrolysis between steel anodes and lead cathodes. At the anode Prussian blue (§ 308) is formed, which is treated for potassium cyanide; the gold is deposited at the cathode (§ 246). This gold is separated from the lead it contains by cupellation.

[Particularly in the United States two processes (chlorination and cyanide) are in general use for extracting gold from its ores without amalgamation. Both processes are especially applicable to low-grade and sulphurous ores, e.g. the tellurides of Colorado. In the *chlorination process* the ore is crushed and roasted and then treated in revolving barrels with chlorine, prepared either chemically or electrolytically, after which the gold is precipitated with hydrogen sulphide and roasted. The *cyanide process* is much similar to that described above for treating the tailings, but zinc generally serves as the precipitant instead of electrolysis.

Placer and *hydraulic mining* find application in newly discovered deposits but are much less common than *vein mining*. For the present status of the metallurgy of gold as well as other metals the student should consult a mining annual.—Tr.]

249. *Physical Properties.*—When pure, gold is reddish yellow, very soft, (much like lead) and extremely malleable and ductile. The thinnest gold-leaf appears green in transmitted light. Sp. g. = 19.265 at 13°. It is a very good conductor of heat and electricity. At 1064° it melts to a greenish liquid.

Chemical Properties.—Gold is the typical representative of the precious metals; it is not attacked by acids and is dissolved only by chlorine-water, aqua regia and potassium cyanide solution (see above). Its compounds are all very unstable; on warming they decompose, leaving the metal.

Uses.—About one-half the world's production of gold is used for industrial purposes. For these purposes the pure metal is too soft, however, and must be alloyed with copper or silver. The proportion of gold in the alloy is ordinarily expressed in *carats;* the pure metal is 24 carats; gold jewelry, etc., usually 14–18 carats i.e., 24 parts of the alloy contain 14–18 parts of gold. The gold coins of the United States contain 1 part copper to 9 parts gold, those of England 1 part copper to 11 parts gold.

For purposes of *gold-plating* the same electrolytic processes are employed as for silver-plating.

Testing of Gold and Silver.

The oldest method of testing is by means of the *touchstone*, or "Lydian stone," a black basalt. This stone must be dull black, unaffected by aqua regia and somewhat rough. The sample is rubbed on the surface of the stone so as to leave a bright streak of particles of the metal. This streak is then compared with that of a series of *touchneedles* of known composition.

Silver streaks are compared merely as to color. A skilled observer can usually estimate the proportion of silver to within 2.0–1.5%.

In the case of gold objects it must be known whether the metal contains copper, silver, or both. Therefore the color of the streak is compared with that of touchneedles of the presumably corresponding alloy. The streaks are then moistened with a little acid consisting of 1 part HCl, 80 HNO_3 and 100 H_2O. Alloys with 75% or more gold are not attacked by this mixture at ordinary temperatures. If the percentage is less, it is possible to detect differences of 1%. This method is decidedly crude and is usually employed only in confirming a supposed percentage. Where the metal is rich it is very deceptive; but gold of a quality such as is generally used for ornaments, etc. (ca. $\frac{583}{1000}$ fine) can be safely tested in this way.

A far more reliable test of the quality of gold is by cupellation. Part of the sample is fused with lead in a small muffle furnace in a small thick-walled, porous crucible (cupel) consisting of bone ash. At the high temperature of the furnace the lead and any copper present are oxidized and their oxides melt and are absorbed by the bone-ash. As soon as they are completely taken up the brilliant surface of the metal suddenly appears with splendid effect (*brightening* of gold). The residual drop of metal is an alloy of only gold and some silver. The latter is got rid of with boiling nitric acid, after the alloy left on the cupel has solidified and been hammered flat.

The proportion of silver in silverware is now determined exclusively in the wet way, by titration.

250. Gold forms two series of compounds analogous to the oxides Au_2O, *aurous oxide*, and Au_2O_3, *auric oxide.*

Aurous Compounds.

Aurous oxide, Au_2O, is obtained by treating the aurous chloride with dilute potassium hydroxide. It is a dark violet powder, which breaks up into its constituents at 250°.

Aurous chloride, $AuCl$, is produced by heating auric chloride to 185°. It is white and insoluble in water. When heated it splits up into its elements. On being warmed with water it yields $2Au$ and $AuCl_3$.

Aurous iodide is formed (like cuprous iodide) on treating a solution of the chloride with potassium iodide.

The gold double cyanide, $KCN \cdot AuCN$, is prepared by dissolving auric oxide in potassium cyanide; it is used in gold-plating.

Of the oxy-salts of aurous oxide only a few double salts are known.

Auric Compounds.

Auric chloride, $AuCl_3$, can be obtained by dissolving gold in aqua regia or by the action of chlorine on the metal. It forms a dark red crystalline mass, which deliquesces rapidly. On the evaporation of its solution it partially decomposes into chlorine and aurous chloride. By evaporating with hydrochloric acid long yellow needles are obtained, consisting of a compound $AuCl_3 \cdot HCl$, which can be regarded as *chlor-auric acid.* Many salts of this acid are known to exist, e.g. $KCl \cdot AuCl_3 + 2\frac{1}{2}H_2O$ and $NH_4Cl \cdot AuCl_3 + H_2O$, as well as many chlor-aurates of organic bases. These double salts give the ordinary tests for gold, hence this acid either forms no complex ion $AuCl_4'$ or is very unstable. Auric chloride is also soluble in alcohol and in ether.

Auric oxide, Au_2O_3, can be prepared by precipitating auric chloride with magnesia. The latter can be removed from the precipitate with concentrated nitric acid, the auric oxide remaining as a brown powder, which breaks up at 250° into its elements.

If the precipitate produced by magnesia is treated with dilute nitric acid, a reddish-yellow powder of the formula AuO_3H_3 is obtained, which displays acid, instead of basic, properties. Salts of this **auric acid** are known, which are derived from the compound $Au(OH)_3 - H_2O = AuO \cdot OH$. Potassium aurate, for example, has the formula $KAuO_2 + 3H_2O$ and crystallizes in yellow needles. Many other salts are also known; the above-mentioned precipitate with magnesia, for example, can be looked upon as the magnesium salt of auric acid, $Mg(AuO_2)_2$.

Auric sulphide, Au_2S_3, is precipitated from gold solutions by hydrogen sulphide. It is very dark brown and soluble in ammonium sulphide.

Gold is precipitated from its solutions in the metallic form by various reducing agents. Ferrous sulphate (§ 248), oxalic acid and acetylene water serve very well for this purpose. Hydrogen peroxide precipitates gold quickly in alkaline solution.

251. For many centuries the *alchemists* endeavored to produce gold from the baser metals. It is needless to say that their efforts were never rewarded. The chances of this hope being realized must at present be regarded as very slight, since gold is an element. Inasmuch, however, as our conception of an element is relative (§ 8), i.e. it depends on the extent of our mastery over natural forces, the impossibility of decomposing gold or synthesizing it from other elements is by no means absolutely established. (See § 267).

Although we now ascribe to every metal fixed, unalterable properties, it might well have seemed possible to the alchemists, with their more limited knowledge, that the properties of the metals could vary. None of the metals except gold occur pure in nature; they have to be extracted from oxides or sulphides, which frequently contain various impurities. The metals thus obtained had no definite properties; distinction was made between various sorts of lead, copper, etc. The mutability of the metals may be said to have been the first principle which observation taught; indeed, when a piece of metal is fused with small amounts of various other substances, its properties (color, etc.) really do change. Moreover, at the time of the alchemists the present concept "element" was not yet established; this was first introduced by BOYLE (1627–1691). Before then, the doctrine of ARISTOTLE was very generally accepted, according to which all substances are made up of air, fire, earth and water. In order to produce gold it therefore seemed only necessary to deprive the baser metals of certain properties and substitute others. As to the metals themselves the idea was prevalent in alchemistic circles that mercury was the primordial substance and that it had undergone various changes. Before gold could be made from it it must be made refractory and of a yellow color. Not a few alchemists were convinced, moreover, that the success of the "great work" depended on the coöperation of a higher power.

SUMMARY OF THE GROUP.

252. The metals copper, silver and gold form a bridge from the difficultly fusible metals, Ni, Pd, Pt (Group VIII), to the easily fusible, Zn, Cd, Hg (Group II); their melting-points are between those of the two groups. The following brief table summarizes the physical constants of these metals as well as those of the related elements, lithium and sodium:

	Li	Na	Cu	Ag	Au
Atomic weight	7.03	23.05	63.6	107.93	197.2
Specific gravity	0.59	0.97	8.94	10.5	19.33
Melting-point	180	97.6	1050	954	1200
Color	white	white	red	white	red

The analogy in the chemical properties is chiefly apparent in the *-ous* compounds. These have the type R_2O for the oxygen compounds and RX for the halides. The *-ous* halides of Cu, Ag and Au are all white and insoluble in water; they are isomorphous with sodium chloride.

Moreover, there are certain analogies in solubility. Lithium carbonate and hydroxide are less soluble in water than the corresponding sodium compounds; copper carbonate and hydroxide are insoluble, while the corresponding silver compounds dissolve to some extent. The sulphate of sodium (third horizontal series) crystallizes preferably with $10H_2O$, that of copper (fifth series) with $5H_2O$, while silver sulphate (seventh series) is anhydrous.

The oxygen compounds exhibit a gradual decrease in stability. Li_2O and Na_2O are unaffected by high temperatures, but CuO is transformed into Cu_2O, and the oxides of silver and gold break up even at comparatively low temperatures into their elements.

However, it must be admitted that the analogy between these elements is not so great as in other groups. Their difference in valence is especially striking and, moreover, there is little similarity in the properties of the higher stages of oxidation. This is one of the weak parts of the periodic system.

BERYLLIUM AND MAGNESIUM.

I. Beryllium (Glucinum).

253. This is one of the rarer elements. It occurs in the mineral *beryl*, $Al_2O_3 \cdot 3SiO_2 + 3(BeO \cdot SiO_2)$; that variety of beryl which is colored green by traces of a chromium compound is the gem called *emerald*, or *smaragd*. *Chrysoberyl* has the composition $BeO \cdot Al_2O_3$.

Almost all the beryllium compounds are made from beryl. This is disintegrated by fusing with potassium carbonate. The fused mass, after cooling, is treated with sulphuric acid to precipitate the silica. Most of the aluminium is then removed by crystallization in the form of alum, as this is sparingly soluble in cold water, while beryllium sulphate remains in the mother liquor. The latter is then mixed with a hot solution of ammonium carbonate to precipitate aluminium and iron, beryllium still remaining in solution. After acidifying with hydrochloric acid, the beryllium is precipitated as the hydroxide by ammonia

The metal was obtained by heating the double fluoride $BeF_2 \cdot 2KF$ with sodium. It is a malleable solid with the specific gravity 1.64. It does not decompose water, even at 100°. At ordinary temperatures it is permanent in the air. Hydrochloric and sulphuric acids dissolve it readily with the evolution of hydrogen; dilute nitric acid does not attack it so readily. Beryllium is also dissolved easily by caustic potash and soda with the evolution of hydrogen and the formation of salts having the formula $Be(OR)_2$. The hydroxide thus behaves as a weak acid towards strong bases. These properties correspond to those of aluminium; in § 215 attention was already called to the analogy between these two elements. This analogy also characterizes their compounds, e.g., beryllium carbide yields pure methane with water, just like aluminium carbide (§ 178).

Only one **oxide** of beryllium is known, BeO (§ 215). It is a white powder, which after ignition is difficultly soluble in acids (like Al_2O_3). It is obtained by heating the hydroxide, $Be(OH)_2$, which is precipitated from solutions of the salts as a white gelatinous mass. When freshly precipitated, it is easily soluble in alkalies, ammonium carbonate and dilute acids. On being heated with water, dilute ammonia solution or dilute alkali solution, or on being ignited, or even on standing for some time, it "grows old" and loses these properties. Heating with ten-fold normal solution of an alkali hydroxide "rejuvenates" even the "oldest" beryllium hydroxides, which are dissolved only slowly by warm concentrated hydrochloric acid. Beryllium hydroxide is distinguished from aluminium hydroxide in two respects: it dissolves in ammonium carbonate (see above) and is precipitated from the solution in caustic soda or caustic potash by prolonged boiling.

Beryllium sulphate, $BeSO_4$ crystallizes with four or seven molecules of water, in the latter case being isomorphous with $MgSO_4 \cdot 7H_2O$. The double salt $BeSO_4 \cdot K_2SO_4 \cdot 3H_2O$ is (like alum) sparingly soluble in cold water. **Beryllium chloride,** $BeCl_2$, must be prepared from the oxide by heating with charcoal in a current of chlorine. Its vapor density corresponds to the formula $BeCl_2$. It crystallizes with $4H_2O$. **Beryllium carbonate** is soluble in water. It loses carbon dioxide very easily.

The beryllium salts taste sweet, hence the name glucinum (or glycinium), which is common in France and America.

II. Magnesium.

254. This element occurs as carbonate, silicate, and chloride in considerable quantities. *Magnesite* is $MgCO_3$, *dolomite* $MgCa(CO_3)_2$. Among the silicates containing magnesium we have *talc* and *soapstone*, $H_2Mg_3Si_4O_{12}$; *serpentine* (*asbestos*), $H_4Mg_3Si_2O_9$; *meerschaum*, $H_4Mg_2Si_3O_{10}$. It is found in smaller amounts in many other silicates, e.g. *hornblende* (*asbestos*), *augite*, *tourmaline*. Other salts found in nature are *carnallite*, $MgCl_2 \cdot KCl \cdot 6H_2O$, *kieserite*, $MgSO_4 \cdot H_2O$, and *kainite*, $MgSO_4 \cdot KCl \cdot 3H_2O$ (*Stassfurt Abraum salts*). Upon the weathering of the silicates the magnesium goes into the soil, whence it is absorbed by the plants (to which this element is invaluable) and finally taken into the animal body.

The metal is manufactured on a large scale, since it is employed for illumination in photography, pyrotechnics, etc., on account of the intense light (*flash-light*) produced by its combustion. At present it is prepared mainly by the electrolysis of fused magnesium chloride or carnallite in a cast-steel crucible, which serves as cathode; gas carbon is used for the anode. It is also obtained by heating the double chloride $MgCl_2 \cdot NaCl$ with sodium. It is silvery-white and has a high lustre. Sp. g. = 1.75. It is malleable and ductile and comes on the market in the form of wire or ribbon as well as powder, but the ribbon frequently contains zinc. It melts at 800° and distils at red-heat. It is quite permanent in the air, since it soon becomes coated with a thin cohesive film of the oxide; at an elevated temperature it burns to magnesia, MgO. When it is heated red-hot in a limited supply of air, a large part is converted into the nitride, Mg_3N_2, a yellowish-green substance. Boiling water decomposes it slowly with the evolution of hydrogen. It dissolves readily in acids but is unaffected by alkalies. It is a powerful reducing-agent, reducing silica (§ 190), for example; moreover, when ignited, it burns in water vapor.

Magnesium oxide, MgO, *magnesia,* is the only oxide of magnesium known. It results from the combustion of the metal or from heating the hydroxide or carbonate. It is a white, very light powder, which is employed in medicine under the name *magnesia usta.* With water it forms the hydroxide $Mg(OH)_2$.

Magnesium hydroxide, $Mg(OH)_2$, is precipitated from solutions of magnesium salts by alkalies. It is slightly soluble in water and turns red litmus blue; however in an excess of alkali its ionization is so diminished that it becomes practically insoluble. It is a weak base, but is strong enough to absorb carbon dioxide from the air. It dissolves readily in an aqueous solution containing ammonium salts. According to OSTWALD, this is to be explained as follows: The solution of an ammonium salt contains a large quantity of NH_4-ions. When a substance is introduced into the solution, which gives off OH-ions, as does magnesium hydroxide, these NH_4-ions unite with OH-ions to form NH_4OH, or rather NH_3+H_2O (*cf.* § 234). As a result of this reaction OH-ions disappear. In order to restore the equilibrium between the undissolved magnesium hydroxide and the solution, more of this hydroxide must go in solution, but again the freshly formed OH-ions are taken up by the NH_4-ions. If sufficient of the latter are present, this process will go on till all the magnesium hydroxide has entered into solution. It now becomes clear why, on the other hand, the solution of a magnesium salt is not precipitated by ammonia in the presence of a sufficient quantity of ammonium salt.

MAGNESIUM SALTS.

255. **Magnesium chloride,** $MgCl_2$, crystallizes with six molecules of water and is very hygroscopic. The deliquescence of common salt is due to the magnesium salt it usually contains. For the rôle of this salt in the Solvay process compare § 226, 2. On evaporating the aqueous solution the basic chloride, $Mg{<}^{OH}_{Cl}$, and hydrochloric acid are formed; sea-water cannot be used in boilers because of the magnesium salt it contains, for the hydrochloric acid set free attacks the iron. Many double salts of magnesium chloride are known.

It can be obtained anhydrous by heating the double chloride

$MgCl_2 \cdot NH_4Cl \cdot 6H_2O$, when it forms a laminar-crystalline mass, which melts at 708° and distils without decomposition at bright red heat.

Magnesium sulphate, $MgSO_4 \cdot 7H_2O$, *Epsom salt,* finds use in medicine. It is very soluble in water. It loses 6 mols. H_2O at 150°, and the seventh above 200°. In this respect it behaves like other sulphates, e.g. $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, and those of nickel and cobalt, which are, moreover, isomorphous with it. A further analogy between these sulphates appears in the fact that with sulphate of potassium or ammonium they form double salts of the same type, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, which are also isomorphous.

Magnesium ammonium phosphates, $MgNH_4PO_4 \cdot 6H_2O$, serves for the precipitation of magnesium as well as of phosphoric acid. It is not wholly insoluble in water, but does not dissolve in ammonia, the reason for which is again to be found in the reduction of the ionization. Completely analogous to this compound is the corresponding arsenate, $MgNH_4AsO_4 \cdot 6H_2O$.

Magnesium carbonate.—From solutions of magnesium salts soda precipitates a basic carbonate, $Mg(OH)_2 \cdot 4MgCO_3 \cdot 4H_2O$. The carbon dioxide liberated holds part of the magnesium in solution as acid carbonate. This precipitate is known as *magnesia alba.* The neutral carbonate can be prepared from it by suspending magnesia alba in water, passing in carbon dioxide and allowing to stand; in time the salt $MgCO_3 \cdot 3H_2O$ crystallizes out, which is, however, readily split up hydrolytically by water, forming basic carbonate again.

CALCIUM, STRONTIUM AND BARIUM.

I. Calcium.

256. This element is one of the ten principal constituents of the earth's crust (§ 8). Particularly the carbonate is found in large quantities in nature, *limestone, calcite, aragonite, marble* and *chalk,* all being forms of it. An earthy deposit containing a certain amount of calcium carbonate is termed *marl.* Calcium silicates and especially calcium double salts constitute the major portion of the siliceous rocks. There are also extensive beds of calcium phosphate, *phosphorite, apatite,* etc., particularly in Spain and Florida. Calcium occurs as sulphate in the form of *gypsum* and *alabaster.* Moreover, in the animal kingdom large quantities of this element are found. The skeletons of vertebrates are chiefly phosphate and carbonate of calcium; the shells of mollusks consist of calcium carbonate, as do also egg shells. As for the plants, lime is one of their invaluable inorganic constituents.

Metallic calcium can be obtained either by electrolysis of fused anhydrous calcium iodide or by decomposition of the same salt with sodium at red-heat. If an excess (three times the theoretical amount) of sodium is taken in the latter operation, the calcium dissolves in the molten sodium and crystallizes out on cooling. The sodium can be removed with absolute alcohol, which acts on calcium only slightly at ordinary temperatures. Calcium is a silvery-white metal, which melts at 760°; it is soft enough to cut and is malleable, but less so than potassium and sodium; it has a crystalline fracture. Sp. g. = 1.78–1.87. It is relatively little affected by oxygen, chlorine, bromine and iodine, all of which react with the metal only at a higher temperature than the ordinary one. In a current of air calcium unites with both oxygen and nitrogen (§ 110).

OXIDES AND HYDROXIDES OF CALCIUM.

257. **Calcium oxide,** CaO, (quick-lime, unslaked lime) is prepared commercially by "burning" limestone or mollusk shells. The limestone is mixed with coal and the latter is set on fire; the heat of the burning coal decomposes the carbonate of lime into calcium oxide and carbon dioxide. The kilns are usually constructed in such a way that the burned lime can be drawn out at the bottom while the mixture of fuel and limestone is fed in at the top, so that the process is continuous. In the United States "long-flame" periodic kilns are generally used because they are simpler and fuel is inexpensive.

Calcium oxide is a white amorphous powder, which requires the temperature of the electric furnace for fusion (§ 176). On being heated strongly with an oxy-hydrogen flame it emits an intense white light (§ 13). It absorbs water and carbon dioxide from the air; as a result the chunks of lime, which are hard and solid when they come from the kiln, gradually crumble to fine powder.

Calcium hydroxide, $Ca(OH)_2$, (slaked lime) is obtained by "slaking" quick-lime with water. Its formation is attended by the evolution of much heat. It is only sparingly soluble in water (forming *lime-water*), but more soluble in cold water than in warm. The solubility, is however, sufficient to make the precipitation of this hydroxide by ammonium hydroxide impossible, for the concentration of the hydroxyl ions of the latter is too small together with that of the calcium ions present to reach the value of the solubility product of calcium hydroxide. At red-heat it is reconverted into the oxide.

Mortar.—Calcium hydroxide is used in masonry. For this purpose quicklime is mixed with water and sand so as to form a thick paste, called mortar, which is thrown in between the stones. After some time the mass becomes as hard as stone; this is due to the conversion of the hydroxide into the carbonate by the action of the carbon dioxide of the air. The sand makes the mass porous, so that the process of hardening extends inward; the older the wall the harder the mortar. The formation of calcium silicate appears to play only a minor rôle in this process.

If the lime contains more or less magnesia it is difficult to slake; it is therefore less adapted to masonry purposes and is called "poor," or "lean," in contrast with the pure, easily slaked "fat" lime.

Cement contains, besides lime (50-60%), principally silica (*ca.* 24%) and alumina (*ca.* 8%). It is made by burning a mixture of limestone, clay and sand. In some places, e.g. Brohlthal in the Rhine region, such a mixture occurs as "tuffstone," which yields cement directly on burning. Cement after being mixed with water sets very firmly in a short time; this is due, in all probability, to the fact that on treating it with water calcium aluminate is dissolved and the solution slowly deposits a hydrous aluminate, which is much less soluble and causes the setting of the cement. At the same time insoluble calcium aluminium silicates are formed.

Calcium peroxide, $CaO_2 \cdot 8H_2O$, is deposited when lime-water is treated with hydrogen peroxide solution. It gives up oxygen on heating.

SALTS OF CALCIUM.

258. Calcium chloride, $CaCl_2$, is obtained by dissolving the hydroxide or carbonate in hydrochloric acid. It can crystallize with various amounts of water. The hydrate $CaCl_2 \cdot 6H_2O$ forms large crystals. Calcium chloride is very hygroscopic and is therefore frequently used to dry gases or to absorb water dissolved in organic liquids (ether, carbon disulphide, etc.). It melts at 719°. It unites with ammonia to form $CaCl_2 \cdot 8NH_3$; hence it cannot be used to dry this gas.

When crystallized calcium chloride is mixed with ice the temperature falls considerably, even reaching −48.5°. Such a mixture is called a *cooling-* or *freezing-mixture* and is often employed for producing low temperatures. Besides calcium chloride and ice, many other such mixtures are known; the one most frequently used is that of common salt and ice, with which a temperature of −21° can be obtained. Ice is not absolutely necessary; for instance, if solid ammonium nitrate is added to its own weight of water, a temperature of −15.5° can be produced.

In order to understand why such mixtures become so cold we must recall § 237. Suppose that ice is introduced into a saturated salt solution of 0°, solid salt being present at the bottom so that the liquid remains saturated. The system *solution* + *ice* is not in a state of equilibrium at 0°, for the salt solution has a freezing-point much lower than 0°. It cannot therefore continue in this state, but, if it is to be in equilibrium with ice as solid phase, the temperature must sink, and this is only possible as the ice melts, by which process heat is changed into the latent condition. If enough ice is present, it can, by melting, continue to withdraw free heat from the system till the cryohydric point is reached; for only at or below that point can ice and salt exist permanently side by side. It follows, therefore, that the cryohydric temperature is the lowest that can be reached by the mixture. In § 237 it was shown, further, that there is no essential difference between the two components of a solution; this is also seen on considering cooling-mixtures containing no ice. For instance, when ammonium nitrate is added to water, the solution has a freezing-point much lower than 0°. Here it is the great absorption of heat in dissolving the salt, that causes the fall of temperature necessary to establish the equilibrium. If this fall is to be considerable, the solubility of the salt must of course be great. In this case also the cryohydric point is the lowest temperature that can be reached by the mixture.

Chloride of lime is a name given to a product obtained by saturating slaked lime with chlorine at ordinary temperatures. Just what compound is formed here is not yet definitely known although the matter has been frequently investigated. There is, however, much evidence in favor of the formula $\mathrm{Ca}<{\mathrm{OCl} \atop \mathrm{Cl}}$, according to which it is a mixed salt of hydrochloric and hypochlorous acids. At any rate this is more probable than the supposition that chloride of lime is a mixture of calcium hypochlorite and calcium chloride (§ 56), for it is not possible to extract any chloride of calcium from it with alcohol, although this salt is very soluble in alcohol, and almost all the chlorine is expelled by a current of carbon dioxide.

Chloride of lime is employed in large quantities for bleaching and disinfecting (*bleaching-powder*). It is an incoherent white powder with the odor of chlorine (on account of decomposition by the carbon dioxide of the air.) When treated with hydrochloric or other acids it yields chlorine:

$$\mathrm{Ca}{\mathrm{OCl} \atop \mathrm{Cl}} + 2\mathrm{HCl} = \mathrm{CaCl_2} + \mathrm{H_2O} + \mathrm{Cl_2};$$

$$\mathrm{Ca}{\mathrm{OCl} \atop \mathrm{Cl}} + \mathrm{H_2SO_4} = \mathrm{CaSO_4} + \mathrm{H_2O} + \mathrm{Cl_2}.$$

A solution of chloride of lime, when mixed with a cobalt salt and warmed, evolves oxygen. This reaction can be regarded as primarily an oxidation of CoO to Co_2O_3, the latter then yielding oxygen with chloride of lime and forming CoO anew. The cobaltous oxide would thus act as a catalyzer.

Calcium fluoride, CaF_2, occurs in nature as *fluor spar* or *fluorite*, forming cubes, which are often fluorescent. It is insoluble in water. It fuses at red-heat and is frequently employed as a flux in metallurgical processes. It can be obtained artificially by treating a solution of calcium chloride with sodium fluoride, NaF.

Calcium sulphate, $CaSO_4 \cdot 2H_2O$, occurs in nature as *gypsum* (§ 256). It is only slightly soluble in water. We also find calcium sulphate in nature as *anhydrite*, which has no water of crystallization and is very difficultly soluble in water. Gypsum passes over into this anhydrous modification on being ignited. However, the reverse transformation, recombination with water, does not take place, or at least proceeds very slowly, so that ignited gypsum is said to be "dead-burnt." If the dehydration is carried out at a lower temperature, an anhydrous gypsum is obtained which is comparatively easily soluble in water ("soluble anhydrite") and absorbs water very rapidly. In addition to these varieties there is also a "half-hydrate", $2CaSO_4 \cdot H_2O$. This is the chief constituent of "plaster of Paris." On being stirred with water it takes up the latter rapidly and, like the soluble anhydrite, forms the dihydrate, $CaSO_4 \cdot 2H_2O$, whereupon the mass becomes hard. This is the basis of the application of gypsum in the manufacture of casts, etc.

The "setting" depends upon the relatively high solubility (about 1%) of this half-hydrate, on account of which it forms a solution supersaturated as to gypsum ($CaSO_4 \cdot 2H_2O$; solubility about 0.2%) and gypsum is deposited. Another very essential factor in the setting is the filamentary character of the precipitated gypsum, a property which is entirely lacking in the case of calcium hydroxide, for which reason slaked lime does not hold together.

The credit of having explained the conditions governing the existence of the above-mentioned modifications as well as of having determined the positions of their transition points is due to VAN 'T HOFF. The investigation was rendered the more difficult because of the retardation phenomena which obscure the true situation. It was found that the half-hydrate is to be regarded as a metastable modification, because, for one reason, the temperature at which it goes over into soluble anhydrite is lower than that at which the dihydrate loses all its water, while in general the loss of water by hydrates proceeds step by step with rising temperature. Moreover the greater solubility of the half-hydrate, as compared with that of the dihydrate, is an additional reason. There is thus the same relationship here as between the metastable crystals $Na_2SO_4 \cdot 7H_2O$ and the salts $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4, except that in this latter case the transformation from metastable to stable modification takes place very easily on touching the heptahydrate with a crystal of the decahydrate, while the half-hydrate of calcium sulphate, even in contact with the dihydrate, retains its identity indefinitely.

Calcium nitrate, $Ca(NO_3)_2$, results from the decay of nitrogenous organic substances in the presence of lime. It crystallizes with four molecules of water. The anhydrous salt deliquesces in the air and dissolves readily in alcohol. It is converted into saltpetre by potash or potassium chloride (§ 229).

Calcium phosphates.—The *tertiary* salt, $Ca_3(PO_4)_2$, is insoluble in water, as is also the *secondary* salt, $Ca_2H_2(PO_4)_2$, The *primary* salt, $CaH_4(PO_4)_2$, however, is readily soluble; it is employed in large quantities as an artificial fertilizer, under the name of "superphosphate."

This superphosphate is manufactured by thoroughly mixing ground phosphorite (or bone meal) in a cast-iron mixer with chamber acid according to the proportions of the equation

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

The mass, which is at first semi-solid, soon becomes solid, since the calcium sulphate that is formed takes up the water contained in the chamber acid to form crystals.

When superphosphate is mixed with soil the primary calcium sulphate goes into solution and, since every soil contains lime, it is forthwith reconverted into insoluble secondary or tertiary phosphate. Apparently nothing has been gained toward "making the phosphoric acid soluble." However the phosphate is now diffused widely in the soil and is therefore much more accessible to the roots of the plants than if the soil had been mixed with tertiary phosphate only.

259. Calcium carbonate, $CaCO_3$, is dimorphous, occurring rhombohedral as *calcite* and rhombic as *aragonite*. When the solution of a calcium salt is treated with soda, calcium carbonate is at first precipitated in an amorphous, very voluminous and more soluble form; after a short time, however, it turns to a finely crystalline powder. It is very slightly soluble in water, but more extensively so in water containing carbonic acid, since the acid calcium carbonate is then formed. The latter decomposes when the solution is boiled, carbon dioxide escaping and crystalline neutral carbonate being deposited.

Hardness of Water.—Almost every river- or spring-water holds more or less lime in solution. The lime is present as sulphate or as acid carbonate. Such a water forms but little, if any, lather with soap; the fatty acids of the soap form white insoluble salts with the lime, so that water containing much lime is not good for washing. Such a water is termed hard in contrast with a water that is free or nearly free from lime, which is called soft. If the hardness is due to acid carbonate (also called "bicarbonate" of lime), it disappears on protracted boiling, calcium carbonate being precipitated. In such a case we speak of temporary hardness. In metallic boilers and similar vessels the carbonate, of lime that is deposited adheres firmly to the sides ("boiler-scale"). If the hardness of a water is due to gypsum, which is only partially removed by boiling (§ 236), it is spoken of as permanent hardness.

When heated, calcium carbonate breaks up into lime and carbon dioxide. We have here a case of complete heterogeneous equilibrium (§ 71), for the susbtances are CaO and CO_2 and the phases CaO, $CaCO_3$ and CO_2. This is confirmed by experiments, which show that the concentration of the gaseous phase (the dissociation tension) at a definite temperature is constant and therefore independent of the amount of each phase. Complete decomposition into lime and carbon dioxide can only occur, therefore, when the gaseous phase is removed (as in lime-burning, § 257) or when its tension is kept below the dissociation tension. On the other hand, if the tension of the carbon dioxide is greater than the dissociation tension, calcium carbonate cannot decompose. Under these circumstances it is possible to fuse calcium carbonate; on solidification it assumes a crystalline structure and becomes *marble*.

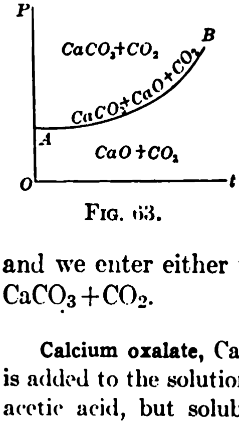


FIG. 63.

In the adjoining Fig. 63, let *AB* represent the dissociation curve of calcium carbonate in a coördinate system *Pt*. Only along this curve are the three phases in equilibrium with each other; under any other conditions one of the phases disappears and we enter either the region of the phases $CaO+CO_2$ or that of $CaCO_3+CO_2$.

Calcium oxalate, $CaC_2O_4 \cdot 2H_2O$, is deposited when ammonium oxalate is added to the solution of a calcium salt. The precipitate is insoluble in acetic acid, but soluble in mineral acids. This is a good illustration of the statement in § 146 that those salts which are insoluble in water dissolve only in acids that are stronger than the acid of the salt. According to their conductivities acetic acid is less ionized, and the strong mineral acids more ionized, than oxalic acid. The addition of the slightly dissociated acetic acid causes only a partial combination of the H-ions and C_2O_4-ions (anions of oxalic acid) so that only very little calcium oxalate has to dissolve before the value of the solubility product is again reached. The addition of a strong mineral acid, however, causes the H- and C_2O_4 ions to unite to such an extent that the solubility product of calcium oxalate can no longer be reached and the latter must therefore dissolve completely.

GLASS.

260. Calcium silicate is chiefly important because it is a constituent of almost all sorts of glass.

Glass is a mixture of silicates of the alkalies with calcium silicate or lead silicate. The alkali silicates are soluble in water, amorphous and easily fusible. The calcium silicates, however, are insoluble, very hard to fuse and frequently crystallized. By fusing both together an insoluble amorphous transparent mass of moderate fusibility is obtained, which is glass. It is prepared by fusing a mixture of clean sand, lime and soda in refractory crucibles.

The properties of glass depend primarily on the quality of the materials and secondarily on the proportions used. By varying these two conditions it is easy to obtain grades of glass varying widely in fusibility, hardness, lustre, refractive power, etc. There are very many different sorts in use. Some of the most important are the following:

Soda glass (*window-glass*) is a soda-lime silicate. It is readily fusible and is used for most purposes of the household.

Potash glass (*crown glass, Bohemian glass*) consists of a silicate of potassium and calcium. It is very difficult to fuse and is therefore extensively used for chemical purposes (combustion tubes, etc.).

Lead glass (*flint glass*) is a silicate of potassium and lead. It is softer, more easily fusible and highly refractive and takes on a beautiful lustre when polished. It is therefore used for optical instruments and fancy glassware ("cut glass").

Besides the substances mentioned many others are used in glass factories to impart particular properties to the glass. The addition of boric acid or the partial replacement of lead with thallium gives lead glass a still higher refractive index. An admixture of alumina, Al_2O_3, prevents or hinders chemical utensils of glass from becoming brittle and allows the replacement of part of the alkali by lime. Certain metallic oxides form colored silicates and are therefore mixed in with the furnace charge to color the glass (cobalt, blue; chromium or copper, green; uranium, yellow-green fluorescent; etc.). The addition of bone-ash, $Ca_3(PO_4)_2$, or tin oxide gives a milky-white opaque glass. The following table shows the percentage composition of various kinds of glass, as determined by analysis:

	SiO_2	K_2O	Na_2O	CaO	PbO	Al_2O_3 and Fe_2O_3
Window-glass	70	....	13	13	....	1
Bottle-glass	60	....	3	25	....	7
Crown glass	73	11.5	3	11	....	1
Flint glass	50	11	....	....	38	0.5

Water has in general very little effect on glass; nevertheless it attacks it somewhat. Old window-panes have a peculiar iridescence, due to surface weathering. As it is very important in exact analyses to know how much glass can be dissolved from the utensils, careful investigations have been carried out, the results indicating the following: When the glass is new a relatively large amount goes into solution; this amount gradually decreases in the course of a few weeks to a minimum. At the first the alkali in particular is dissolved from the surface and the resulting solution then acts as a solvent for the silicic acid. To prepare glass vessels so that they are almost wholly unaffected by water they are subjected to a jet of steam for a quarter of an hour or left for several weeks full of water, the water being renewed occasionally. Thus there is formed on the surface a thin layer, rich in silica and lime, which protects the inner portion from the action of the water.

The dissolving action of water on the alkali of glass can be readily shown by agitating finely powdered glass in water. The liquid at once turns phenolphthaleïn bright red.

Glass is a typical amorphous substance. Such substances are often defined as liquids with a very high internal friction and the behavior of molten glass on cooling is an excellent illustration of this definition. At high temperatures molten glass is a thin liquid; if the temperature is allowed to sink, the consistency of the glass becomes tougher, so that between the wholly liquid and the wholly "solid" states, there is a continuous series of half-liquid states. As it is thus impossible to find a temperature limit to the applicability to glass of the laws of solutions, e.g. the law of diffusion, it seems rational to consider the "solid" amorphous state as liquid, in contradistinction to the crystalline state, which latter is truly solid, having very different properties from liquids.

In glass we have, further, an example of a *solid solution.* By this term VAN'T HOFF understands any solid substance which is a homogeneous mixture, such as a metallic alloy, for example. Crystallized substances can also form solid solutions, or *mixed crystals* (§ 210), as they are commonly called. The term "solid solution" is applied to these solid mixtures, because they are found to have various properties of liquid solutions. For example, a solid solution may become saturated; i.e. at a higher concentration than corresponds to saturation the solid phase becomes heterogeneous.

Calcium sulphide, CaS, is made by heating gypsum with charcoal. On treating the mass with water calcium hydrosulphide, $Ca(SH)_2$, is formed, whose aqueous solution loses hydrogen sulphide on boiling. Calcium sulphide (like the sulphides of barium and strontium) has the property of emitting light in the dark after it has been exposed to sunlight, but seems only to show this phenomenon when it contains traces of other elements, such as vanadium or bismuth.

II. Strontium.

261. This is one of the less widely diffused elements. The principal strontium minerals are *strontianite,* $SrCO_3$, and *celestite,* $SrSO_4$. Its compounds are very analogous to those of calcium.

The metal has been obtained by the electrolysis of fused strontium chloride. Its specific gravity is 2.5. In its properties it corresponds to calcium throughout.

Strontium oxide, SrO, is formed on igniting the hydroxide or carbonate. The temperature required for the complete dissociation of the latter is higher than that for the corresponding calcium compound. The **hydroxide,** $Sr(OH)_2 \cdot 8H_2O$, is more soluble in water than calcium hydroxide. The **chloride,** $SrCl_2 \cdot 6H_2O$, is hygroscopic, like that of calcium. It is soluble in alcohol and can, with the aid of the latter, be easily separated from barium chloride, which is insoluble in alcohol. **Strontium sulphate** is much less soluble than calcium sulphate; at 16.1° 1 part $SrSO_4$ dissolves in 10070 parts H_2O ($CaSO_4$, 1 part in 543 at 15.2°). In a mixture of alcohol and water it dissolves to an extremely small extent. Strontium nitrate, $Sr(NO_3)_2$, is insoluble in alcohol; this forms the basis of separating it from calcium nitrate, which dissolves in alcohol.

Strontium salts are used in pyrotechnics because of the beautiful crimson color they impart to a flame.

III. Barium.

262. This element occurs combined as *barite*, or *heavy spar*, $BaSO_4$, and as *witherite*, $BaCO_3$, in considerable quantities. In preparing the other barium salts it is merely necessary to dissolve the latter mineral in the proper acid. Barite, however, must first be reduced by ignition with charcoal. This can be accomplished in the electric furnace:

$$(1)\ 4BaSO_4+4C = BaS+3BaSO_4+4CO;$$
$$(2)\ 3BaSO_4+BaS=4BaO+4SO_2.$$

The metal is, in this case also, obtained by the electrolysis of the fused chloride. Another method is to treat a hot barium chloride solution with sodium amalgam, forming barium amalgam; on distilling off the mercury in a current of hydrogen, the barium is left, although not entirely free from mercury. It decomposes water vigorously even at ordinary temperatures. Sp. g. = 3.75.

Barium oxide, BaO, is obtained by igniting the nitrate or hydroxide at a high temperature. It unites very readily with water to form the **hydroxide,** $Ba(OH)_2$, which is rather soluble in water (yielding *baryta-water*), and crystallizes from the hot solution on cooling in pretty laminæ, which contain eight molecules of water.

Barium peroxide, BaO_2, forms on heating the oxide in a current of oxygen or air. When it is introduced into dilute sulphuric acid, barium sulphate is precipitated and hydrogen peroxide left in solution. If baryta-water is again added, the hydrate $BaO_2 \cdot 8H_2O$ crystallizes out.

Barium chloride, $BaCl_2 \cdot 2H_2O$, is not hygroscopic like the chlorides of strontium and calcium. The **nitrate** crystallizes anhydrous.

Barium sulphate, $BaSO_4$, is characterized by an exceedingly small solubility in water and acids; at 18.4° 1 part dissolves in 429,700 parts H_2O. It is used as a filler and as a pigment under the name of "permanent white," or *blanc fixe.* **Barium carbonate** yields carbon dioxide only at very high temperatures, prolonged heating at 1450° being required for complete decomposition.

SUMMARY OF THE GROUP OF THE ALKALINE EARTHS.

The following small table summarizes the physical properties of the elements of this group:

	Be	Mg	Ca	Sr	Ba
Atomic weight	9.1	24.36	40.1	87.6	137.4
Specific gravity	1.64	1.75	1.58	2.5	3.75
Atomic volume	5.6	13.8	25.2	34.9	36.5
Color	white	white	white	....	....

As to the specific gravity we observe that only in the cases of Ca, Sr and Ba is a steady increase noticeable.

In respect to the chemical properties, it has already been remarked that these elements act only as bivalent; all compounds of the group therefore have the same formula type. In the solubility of the sulphates a gradual decrease is to be observed with rising atomic weight.

Just as in the first group three elements K, Rb, Cs, exhibit a particular kinship, so here calcium, strontium and barium are closely related in their properties, while the two other members of the group are unlike them in many respects. Beryllium displays analogy with aluminium in certain points just as lithium does with magnesium.

SPECTROSCOPY.

263. If the light from an ordinary gas-flame or the WELSBACH incandescent light is broken up by a prism, there is projected a continuous series of perfectly blended colors from red through yellow, green and blue to violet. This phenomenon is called a **spectrum,** and, since it is unbroken, a **continuous** spectrum. We have previously remarked that the luminosity of a gas-flame is due to incandescent solid particles of carbon. It has been found to be a general rule that incandescent solids give a continuous spectrum.

With incandescent gases it is different. If, for instance, we split up the light from a Bunsen flame, in which salts of sodium, calcium or other metals are volatilized, we see only a few narrow bands of light in certain places, the rest of the spectrum being dark. This is termed a **line** spectrum. Every element has its own peculiar *spectrum lines*. If the spectrum of the incandescent vapors of a mixture of elements is carefully examined, it is found to contain all the characteristic lines of each element. Since it is only necessary to volatilize extremely small amounts of substances in order to show their lines, it is readily seen how important the spectrum-analytical methods introduced by Bunsen and Kirchhoff must be.

For the examination of spectra a number of instruments have been constructed, varying according to the particular object in view. For chemical analysis the apparatus of Vogel or that of John Browning is now very generally used. It is a small direct-vision spectroscope which gives a very bright spectrum and has a sufficient dispersion. At the end *B* (see Fig. 64) is the slit which can be made narrower or wider by turning the rim *D*. The small mirror *m* serves to throw light through the hole *P* on to an auxiliary prism, in order to compare the spectrum of the light which is to be analyzed with that of a known source. At the left end is the ocular through which the spectrum is seen. For further information text-books on physics should be consulted.

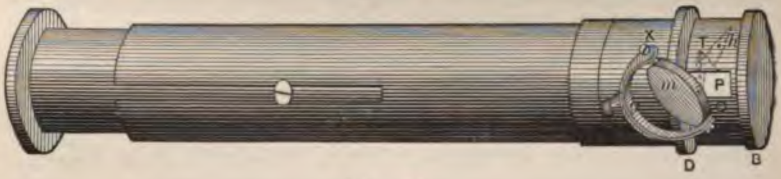


Fig. 64.

In order to examine the spectra of metals it is necessary to convert the latter into the form of vapor at a high temperature. There are different ways of doing this. One is to introduce salts of the metals into a colorless flame by means of a platinum wire. The heat dissociates halogen salts and in the case of oxysalts converts them into oxides, which are reduced to the metallic condition by the hot gases of the flame. This method is very satisfactory for some elements, e.g. those of the alkali and alkaline earth groups, when there is plenty of material. In other cases a *flame spectrum* of this sort is not so good as a *spark* or an *arc spectrum*, for with the latter it is possible to detect with accuracy extremely small amounts of a substance. Other advantages of the latter spectra are their greater light intensity, the greater convenience in execution, and the like. Moreover, at the high temperature here prevailing most elements exhibit spectra which cannot be obtained with the gas-flame.

A spark spectrum can be obtained in a very simple manner, thus: Into the bottom of a little glass cup (*n*, Fig. 65), about 15 mm. wide is fused a platinum wire, which ends in a tube *g* containing mercury and is thus connected with the negative pole of an induction coil; it is incased in a conical capillary tube *x*, beyond which the wire projects about 0.5 mm. At the opposite end is the positive electrode in the form of a platinum wire, which, with the exception of the short end *d*, is fused into a glass tube; the latter is fitted into the cork *a*. If some of the salt solution is poured into the cup about half way up the negative electrode, the liquid is drawn up to the end of *x* by capillarity and every spark volatilizes a tiny portion. In this way there is no loss of material and the sparks are very uniform, so that the observation of the spectrum can be continued at length.

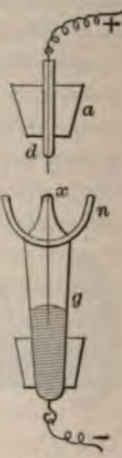


FIG. 65.

For the study of the spectra of substances which are gaseous at ordinary temperatures the PLÜCKER-HITTORF (GEISSLER) tubes are used (Fig. 66). The gases are sealed up in them in a very dilute condition. On connecting one of these with the poles of an induction coil, the whole tube is illuminated most intensely in the narrow portion. This part is placed vertically in front of the slit of the spectroscope.

Some substances have the property of absorbing certain colors and transmitting others. If the solution of such a substance is placed before the slit of a spectroscope and the light of a continuous spectrum allowed to pass through it, dark bands or lines are observed in the spectrum. A number of substances have very characteristic **absorption** spectra.

264. The spectroscope is one of the most delicate means we have of detecting many substances. This is readily seen on considering how small an amount of the substance under examination is volatilized by the sparks. We arrive at numbers like 0.3×10^{-6} mg. sodium, for instance, as the least amount that can be detected. It has thus been possible to discover elements which occur only in company with large amounts of others and would therefore have been very difficult to find in the ordinary way. Bunsen and Kirchhoff themselves found cæsium and rubidium in this way in Dürkheim mineral water. In order to obtain these elements from it in the form of chlorides, it was necessary to evaporate 44,000 kg. water, which yielded 16.5 g. of a mixture of the chlorides. Other very rare elements which were discovered by spectrum analysis are thallium, indium, gallium, ytterbium and scandium.

Fig. 66.

The spectra of the elements differ greatly in appearance, as may be seen at once from Table II (Frontispiece). The numbers indicate wave lengths of light expressed in hundredth microns (10^{-5} mm.). Certain metals, such as sodium, thallium and indium, exhibit only one distinct line when their flame spectra are examined with a spectroscope like the one described above. If a sparking current or an electric arc is employed for the volatilization of the substance and the spectroscope is one giving strong dispersion, many more lines become visible. It is further found on photographing spectra that there are still more lines in the infra-red and ultra-violet portions, which are invisible to the eye. Present-day spectroscopic studies deal, therefore, almost exclusively with carefully prepared photographs.

The number of spectral lines increases rapidly as we proceed to elements of the higher groups of the periodic system. While lithium, sodium and potassium give 20, 35, and 41 lines, respectively, the spectrum of barium contains 163 lines and that of iron more than 5000 lines.

Among these lines there are certain ones which, in virtue of their position (color) and intensity, are specially characteristic of an element, like that of the yellow line in the case of sodium, the green line of thallium and the blue lines of indium. For purposes of identification of such elements these prominent lines are generally observed directly in the spectral apparatus.

Nitrogen is an example of a substance that gives a band spectrum when it is examined in the manner described in § 263.

265. The position of the spectrum lines was formerly indicated numerically according to an arbitrary scale. Now it is expressed with the aid of the wave length λ, 10^{-7} being taken as a unit and the unit being called the ÅNGSTRÖM *unit* after the physicist who introduced it. The wave length of the sodium D_1 line was found to be expressed by 5896.16 such units. The visible part of the spectrum comprises the wave lengths of about 7500–4000 A.U.

Thanks to the researches of ROWLAND, MICHELSON, KAYSER and RUNGE, and others, the wave lengths of a very large number of spectrum lines have been determined with great exactness, so that one is encouraged to attack the question whether in the apparently very promiscuous distribution of lines in the spectra there is such a thing as order.

BALMER was the first to show that this is the case in the hydrogen spectrum. The formula $\lambda = A\frac{m^2}{m^2-4}$, where A is a constant (3646.13) expresses the wave lengths λ of the lines of the spectrum of the element with very close approximation, provided m is substituted by consecutive whole numbers beginning with 3.

The spectra of other elements have been examined for similar regularities, chiefly by RYDBERG and by KAYSER and RUNGE, and it has been found that the regularities are in all of the cases more complex than for the hydrogen spectrum. It would lead us too far to enter upon a discussion of these questions, which properly belong to Physics, but a few of the interesting results are worth mentioning here.

Rydberg, who has devoted particular attention to the spectra of the alkalies, introduced into his formulæ the reciprocal of the wave length, the oscillation frequency n, which represents the number of wave lengths per centimeter. In the spectra of the alkalies he found three series of lines, whose oscillation frequencies can be expressed by the formula

$$n=n_0-\frac{N_0}{(n+\mu)^2}.$$

In this formula N_0 is a constant having the same value for all these metals and all the series; n_0 and μ, however, are two constants that have different values for each series of each metal. For m we substitute again consecutive integers, as in Balmer's formula. This last formula is, moreover, a special case of that of Rydberg, since Balmer's formula can be transformed into

$$\frac{1}{\lambda}=n=n_0'-\frac{N_0'}{m^2}$$

(where $n_0'=A$ and $N_0'=4A$), into which Rydberg's formula is also transformed when $\mu=0$. The values of the constants of these different series were found by Rydberg to have still further definite relationships.

The formula of Kayser and Runge is $\frac{1}{\lambda}=A+Bm^{-2}+Cm^{-4}$, in which A, B and C are constants and m consecutive whole numbers. It represents the wave length of the lines in many cases more faithfully than does the formula of Rydberg; however, there is no relation between the constants A, B and C of the different series.

The spectral lines of the alkalies also exhibit the peculiarity of consisting of double lines (doublets) or triple lines (triplets), the wave-length differences being constant for each series.

Similar series of lines, whose oscillation frequency can be expressed by one of the above formulæ, are found in the spectra of some of the elements. In the spectra of many others, however, they are lacking. In their place we find in the spectra of lead, tin, arsenic, bismuth and others a constant difference between the oscillation frequencies of a considerable number of their lines.

Such investigations as these are prompted by the notion that a knowledge of the laws which govern the distribution of the spectral lines of one and the same substance on the one hand, and the variation in the distribution from substance to substance on the other hand, would throw some light on the nature and kinetic condition of the atoms.

266. With the aid of spectroscopy it has been possible to determine what elements are present in the heavenly bodies. When light from the latter is passed through a prism, line spectra are obtained and these lines correspond in position to those of terrestrial elements. The composition of sunlight has been especially the object of a most extensive study. The spectrum of that body contains numerous black lines, known as FRAUNHOFER lines. The theory of this phenomenon is explained in Optics.

By comparing the FRAUNHOFER lines with the spectra of terrestrial substances it has been found that the sun's atmosphere contains chiefly Fe, Na, Mg, Ca, Cr, Ni, Ba, Cu, Zn and H (the latter in enormous quantity). Moreover, for 450 lines of the iron spectrum there are found to be corresponding dark lines in the sun's spectrum. On the other hand, the solar spectrum displays countless lines which are not yet identified in terrestrial spectra.

267. We are led to presume that many of the elements to which these lines are due will also be revealed on the earth by more careful research, especially when we consider what a small part of the earth is known (see footnote, p. 8). This presumption has been strongly confirmed by the discovery of *helium* (§ 111). The principal line of the latter, D_3—so termed because of its proximity to the double D-line (D_1D_2) of sodium—was observed in the spectra of many fixed stars as well as in that of the sun before the element itself was indentified on the earth. Helium was thus discovered in the stars before it was on the earth. It is a striking fact that it occurs in exceedingly large quantities in the fixed stars (according to spectrometric observations) while there is apparently only a very small amount of it on the earth.

THE UNITY OF MATTER.

The notion that all substances are derived from a single original substance and that the variety that we observe in the material world is merely the result of a difference in arrangement and form of the smallest particles, has long been prevalent. Even the old Greek philosophers had a fondness for it. However, the rise of experimental investigation was not very conducive to the idea. BOYLE (1626–1691) introduced the concept *element* in its present form. According to this concept all substances are to be regarded as elements which, with the means at our command, cannot be further resolved into dissimilar components. The subsequent development of chemistry has shown that the number of these elements is rather large.

Notwithstanding that the idea of a primordial substance lacked substantiation and was more or less discredited, it was by no means rejected, for we have been expressly reminded again and again that the substances which chemistry regards as the simple substances are only classed as elements conditionally; the possibility always remains that a so-called element may be found capable of division into dissimilar components, as has often actually been the case.

Impossible as it was to deny the existence of a primordial substance, the researches of the 18th, and a large part of those of the 19th, century brought to light nothing to support the idea. Not until the discovery of the Periodic System did the question again demand serious attention. This discovery was the first to supply an experimental basis for the assumption of a primordial substance (§ 220). The striking dependence of the properties of the elements on the periodic functions of their atomic weights, which finds its expression in this system, leads of itself to the thought of a fundamental substance, of which the simple substances called elements may be said to be polymers, incapable of resolution by the means at our command.

Another argument for the divisibility of the elemental atoms is contributed by spectroscopy. In order to explain the line spectra exhibited by many elements, we assume that the movements of the atoms give rise to light vibrations of definite wave length, which are perceived by us in the spectral lines. However, since the spectrum of a single element is extremely complicated, we should have to assume that the atoms engender very complex movements. The simplified hypothesis was then offered that it is not the entire atom but smaller particles of which the atoms are composed, that give rise by their vibrations to the different spectral lines.

The physical investigations of the last decade have furnished substantial reasons for believing that the chemical atoms are not in reality the ultimate particles of matter but that they are divisible into particles approximately 2000 times smaller than the hydrogen atom. These particles, carrying with them, as they do, very strong electrical charges, are called "electrons." We cannot in this book do more than indicate the main observations and inferences. The *hypothesis of electrons* is the result of the study of cathode rays in connection with the below-mentioned investigations of radio-active elements. Cathode rays are generated when the discharges of an induction coil are sent through a rarefied gas. It is assumed that from the cathode there are projected particles with strong negative charges, **electrons,** which are propagated with a velocity of several thousand kilometers per second. Accordingly, the cathode rays consist of a stream of these electrons. Measurements of the mass of an electron have shown that it is about $\frac{1}{2000}$ of that of a hydrogen atom. The electrons are the same, whatever gas is contained in the apparatus and whatever electrodes are used, so that we are evidently dealing with a decomposition of the atoms into their ultimate components.

The anions, according to the electron theory, consist of atoms and one or more electrons; the chlorine ion, for example, consists of chlorine and an electron, which latter is represented by θ. The cations are formed from the atoms by the release of one or more electrons. We may thus write:

$$\mathrm{Cl}+\theta=\mathrm{Cl}' \quad \text{and} \quad \mathrm{K}-\theta=\mathrm{K}^{\cdot}.$$

The ionization of potassium chloride in water can be represented by the equation:

$$\mathrm{KCl}_{\mathrm{aq}}=(\mathrm{K}-\theta)_{\mathrm{aq}}+(\mathrm{Cl}+\theta)_{\mathrm{aq}}.$$

Certain physicists presume to be able to go a step further. Some very remarkable investigations of Rowland have shown that a moving electrically charged conductor exerts the same effect as an electric current, so that the latter may be regarded as consisting of very swiftly propagated, discrete electrical particles. Electricity would thus have an "atomistic" structure. FARADAY'S law points in the same direction. According to this law the charges on the ions are either equal to or a multiple of the charge on a hydrogen ion. Fractions of the charge are not found. This is a very significant fact. Just as for the explanation of the analogous laws of DALTON we have assumed that the elements consists of atoms, so we cannot avoid inferring from FARADAY'S law that electricity is divided into discrete elemental particles, which are to be regarded as "atoms of electricity." Furthermore, it has been shown that induction and other phenomena proceed just as if electricity had mass, for electricity has the same properties of inertia as ponderable matter. The consequence is that matter is identified with electricity and the electrons are no longer to be regarded as electrically charged mass particles but as electrical charges themselves, without a material body. These hypotheses would not only unify matter but would also dispel the time-honored notion that energy and matter are distinct.

RADIO-ACTIVE ELEMENTS.

BECQUEREL discovered that uraninite (pitchblende) emits a peculiar sort of rays, which are propagated in a straight line and act on a photographic plate, but are not reflected, refracted or polarized. When gases are traversed by them the gases become electrical conductors. For a while it was questionable whether these properties belonged to uranium or some other substance occurring in uraninite. This mineral is very complex, containing in addition to U_3O_8, a long series of compounds of other metals. We are indebted principally to the CURIES (MR. and MRS.) for the discovery that the emission of these special rays, or the **radio-activity**, is due to the presence of very small amounts of elements, hitherto unknown and of very surprising properties.

The only means of control in the separation of these elements from the other compounds in uraninite after the removal of uranium was to measure the radio-activity of the product obtained in each operation. This was accomplished by measuring the conductivity of a layer of air that was exposed to the rays. Thus after numerous chemical operations the active substance was concentrated more and more. This method is comparable to that employed by BUNSEN and KIRCHHOFF in isolating rubidium and caesium from the Dürkheimer mineral water, where the spectroscope (§ 232) indicated the progress of the concentration of these elements. However, the measurement of radio-activity is many thousand times more sensitive than a spectroscopic examination. Were it not for this fact, the discovery of the radio-active elements would have been impossible, because they occur in such extremely small quantities. For example, 2000 kg. uraninite residues from Joachimsthal yield only about 0.2 g. radium chloride.

Radium is the best known of these elements. It is the only one whose compounds have been obtained in the pure state. It has a characteristic spectrum similar to those of the alkaline earths, and colors the Bunsen flame carmine. In its chemical behavior it shows close analogy to barium; it is separated from the latter element by fractional crystallization of the bromides, radium bromide being more difficultly soluble than the corresponding barium salt (this is true for all the respective salts of the two elements). With the aid of the spectroscope it can be determined whether the salt is entirely free from barium bromide.

The atomic weight of the radium thus purified was found to be 225, which could not be raised by further fractional crystallization. With this atomic weight radium fits exactly into the second group of the periodic system. All radium salts are luminous and excite a large number of substances, such as barium platinocyanide, $BaPt(CN)_4$, uranyl sulphate, precious stones, and the like, to powerful fluorescence. It similarly affects the diamond. Genuine diamonds can thus be distinguished from imitations. The radio-activity of the pure bromide is about a million times that of uraninite.

The rays emitted by radium preparations are of three sorts and are distinguished as α- β- and γ-rays. Quantitatively the first are predominant. All of them have the above-mentioned properties in common; they differ, however, in their penetrating power and in their behavior in the magnetic field. The α-rays are not very penetrating and are only slightly deflected in a strong magnetic field. A sheet of aluminium foil 0.01 mm. thick almost entirely stops their passage. The β-rays are strongly deflected in a magnetic field and consist of rays of various but greater penetrating power, while the γ-rays are scarcely deflected at all and go through obstructions with ease; they form only a small part of the total radiation.

The interesting thing is that these rays are analogous to those generated by electric discharges in highly rarefied gases. The β-rays are to be regarded as cathode rays. They thus consist of negative electrons which are propagated with very great velocity, some almost with the velocity of light (300,000 km. per sec.). From the deflection which they undergo in an electrical field and a magnetic field of known intensity their mass is calculated to be (as in the case of the cathode rays) about $\frac{1}{2000}$ of that of a hydrogen atom. The velocity of these electrons can also be calculated from the same data. Their enormous velocity explains the great penetrating power of β-rays.

The α-rays resemble a sort of radiation which is also obtained by discharging electricity in a rarefied gas, viz., the *canal rays of* GOLDSTEIN. They behave as positively charged projectiles hurled at a great velocity (about $\frac{1}{20}$ of that of light). Their mass is about equal to that of a hydrogen atom, or much greater than the mass of the projectiles formed by the β-rays and the cathode rays. Their greater size and relatively small velocity explains their slight penetrative power.

According to what has been recited in the preceding sections, we are to look upon these forms of radiation as evidencing a **spotaneous decomposition of the atoms** of the element radium. The decomposition is accompanied by a very considerable *evolution of heat.* One gram of radium gives off about 100 g.-cal. per hour; for this reason radium salts have a higher temperature than their surroundings. Even cooling with liquid hydrogen ($-253°$) does not stop this evolution of heat. The magnitude of the heat effect is more apparent upon comparison with other caloric effects attending chemical reactions. We now assume that the heat evolution in the decomposition of 1 g. radium is about 10^9 g.-cal. heat, so that the first-mentioned process gives off 250,000 times more heat than the second.

There are other radio-active substances besides radium. Uranium and thorium are feebly active; **polonium** and **actinium,** which also occur in uraninite, are strongly so. Polonium loses its activity after a few years, but actinium does not. The former is closely allied with bismuth; the latter with thorium. On account of their extremely limited occurence they have not yet been prepared in the pure state. Polonium emits α-rays exclusively.

It has further been observed that air which remains for a long time in cellars and caves acquires an abnormally high conductivity, which can be traced to radio-activity. The ground itself and particularly thermal springs yield an emanation (see below) identical with that of radium. Probably it has its origin in the depths of the earth, where it is perhaps evolved from some radio-active substance or other.

Induced Radio-activity and Emanation.—Every substance that is brought into proximity with a radium salt acquires a temporary, or induced, radio-activity, i.e., it emits the same rays as radium itself. This induced radio-activity is best observed on putting a radium salt in an enclosed space. The enclosing walls, as well as all bodies within the space, become active. It is not the radium rays that cause this effect, for a radium salt in a sealed tube emits rays without exciting any radio-activity. RUTHERFORD discovered the cause of this phenomenon by the observation that there is a constant outflow from radio-active substances, which outflow he calls **emanation.**

Since bodies with induced radio-activity give out rays that are identical with those of radium itself, these rays can be regarded as transformation products of the emanation of radium.

Emanation behaves in many respects as a gas; it diffuses from one vessel into another, follows the law of BOYLE in its compression, can be condensed by cooling with liquid air and volatilized again if the temperature is allowed to rise. Neither physical nor chemical agencies are able to alter emanation. It is indifferent to temperature variation between −180° and 500°, is not absorbed by concentrated acids or alkalies, and can be conducted without change over hot copper oxide. Emanation and induced radio-activity must be considered as intermediate stages in the complete disintegration of the radium atom into the above-mentioned radiations. First in order comes emanation; this in turn breaks up into α- and β-rays and induced radio-activity, of which various sorts are known. However, other substances, part of which have not been further studied, are formed simultaneously. One of them, however, is pretty well known, viz., **helium.** RAMSAY and SODDY have demonstrated that helium is formed in the spontaneous decomposition of radium emanation. The maximum quantity of emanation that could be obtained from 50 mg. radium bromide was conducted by them with the help of an oxygen current into a U-tube cooled by liquid air and the U-tube was then evacuated with a pump. A vacuum tube which was fused on to the U-tube showed no traces of helium after removal of the liquid air. The spectrum appeared to be that of an unknown element—presumably emanation. After the apparatus stood four days the helium spectrum appeared. This phenomenon explains the mysterious persistent occurrence of helium in radium-bearing minerals.

As stated above, emanation and induced radio-activity also disappear in their turn. In the case of each the disappearance follows a definite exponential law. The intensity of the radiation, I, is expressed as a function of the time, t, by a formula:

$$I = I_0 e^{-at},$$

I being the initial intensity of the radiation and e the base of the natural logarithms. In this formula a has a definite value for every decomposition product, the value being independent of the temperature and other conditions. Therefore by determining a we can ascertain what decomposition product is before us. Ordinarily this is simplified in so far as the period is stated at the end of which the intensity of radiation has decreased by half. For the emanation of radium, for example, this period is four days and for its induced radio-activity the period is one hour.

Much interest attaches to the chemical effects that radium preparations can bring about. The most fascinating of all is that discovered by RAMSAY, viz., the **degradation of the elements.**

In the great evolution of heat attending the disintegration of of radium we get an intimation of the immense quantity of energy that is stored up in this element, and that makes this element a source of energy incomparably richer than any other hitherto discovered. This fact has encouraged experimentation to ascertain whether it is not possible with this vast amount of concentrated energy to bring about transformations that have hitherto been considered impossible.

When the emanation of radium is brought into contact with water the latter is broken up into its elements. Strange to say, however, there is an excess of hydrogen, which has varied from 3.6% to 16% in different experiments. Painstaking tests showed that this excess of hydrogen can only come from the water. The spectroscopic examination of the evolved gas revealed further that instead of helium neon had been formed from the emanation. So then, if we allow the energy that is available in emanation to do work, for instance, to decompose a certain quantity of water, a considerable amount of this energy is absorbed and the degradation of emanation does not proceed to its limit, the formation of helium, but stops at the next to the last member of the group of "noble" gases, viz., neon with an atomic weight of 20.

Let us now examine a case where a much greater amount of work is accomplished by the energy available in emanation. When emanation is dissolved in a solution of copper nitrate the solution is eventually found to contain sodium and also lithium. In the gas that comes off neither helium nor neon is found, but argon. These facts are explained in the same way as above. The energy available in emanation has degraded copper to the first member of the family in which it belongs in the natural system, i.e., lithium, probably with sodium, the second member of this family, as an intermediate product. In connection with this great utilization of energy emanation itself is not degraded as far as otherwise; its degradation stops at the third member of the group, argon.

Among the gases that come off spontaneously from an acid solution of thorium nitrate is carbon dioxide. It may thus be conjectured that carbon results from the degradation of thorium at the expense of the energy stored up in this radio-active element, since thorium is the last, and carbon the first, member of the fourth group of the periodic system.

ZINC.

268. The most important zinc minerals are *calamine* ($H_2Zn_2SiO_5$), *smithsonite* ($ZnCO_3$), *sphalerite*, or *blende* (ZnS), and various oxides. The principal localities are Silesia, England, Belgium, Poland, and more recently, certain districts in the United States notably southwestern Missouri. To obtain the metal the ores are roasted—the gas (SO_2) from the sulphide ores is converted into sulphuric acid—yielding zinc oxide. In the older processes this is mixed with coal and heated, forming carbon monoxide and zinc. The latter distils over and collects in the receiver together with a fine gray powder, *zinc dust.* This "dust" is a mixture of zinc oxide and zinc powder and is frequently used in the laboratory as a vigorous reducing-agent.

The metal is bluish-white and has a specific gravity of 6.9–7.2. At ordinary temperatures it is brittle, but at 100–150° it becomes softer; it can then be beaten into plates. At the same time the specific gravity rises to 7.2 and the metal becomes firmer. At 200° it again becomes brittle and can be easily pulverized. It melts at 433° and boils at 920°. The metallic vapor has a specific gravity of 33.8 ($H=1$); hence its molecular weight is 67.6. Since the atomic weight, as deduced from DULONG and PETIT'S law, is 65.4, the molecule in the vaporous state can contain only one atom. The same is true of the related metals cadmium and mercury. Zinc is permanent in the air, since it becomes firmly coated with a protective layer of oxide. Zinc dust decomposes water. When heated to boiling in the air the metal burns to zinc oxide, producing an intensely bright light. It is dissolved very easily by hydrochloric or sulphuric acid with the evolution of hydrogen; it is an interesting fact, however, that when a piece of absolutely pure zinc is placed in either of these acids no hydrogen is generated. If this piece of zinc is brought in contact with a platinum wire, effervescence begins at once, not from the surface of the zinc, however, but from that of the wire, and zinc goes into solution. Written in ions the process is

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + 2H,$$

and its explanation is just the same as that given in § 203, for the formation of a "lead tree." In this case also the zinc drives cations into the solution with great force, itself thus assuming a negative charge, with which hydrogen ions can be discharged. The only difference seems to be that these hydrogen ions discharge themselves at the platinum instead of at the zinc. However, this difference is not real, since in the case of the lead tree the fresh portions of lead are deposited on the outermost parts of it. The perfect analogy is made still clearer by a somewhat modified form of the experiment:

When, on the one hand, a plate of amalgamated zinc and one of platinum are connected by a metallic wire and dipped in dilute sulphuric acid (Fig. 67) hydrogen is evolved from the platinum plate and when, on the other hand, a plate of amalgamated zinc and one of lead are similarly connected and dipped in a dilute solution of lead nitrate (Fig. 68) lead crystals are deposited not on the zinc but on the lead. In both cases the negative charge of the zinc goes through the wire to the other plate, on which the ions of hydrogen, or lead, as the case may be, can discharge themselves.

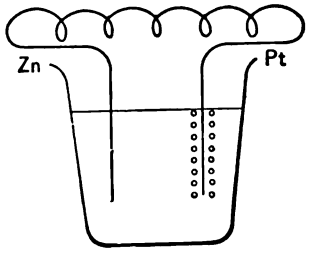


FIG. 67.

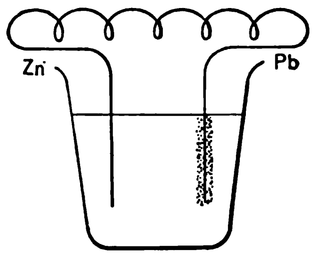


FIG. 68.

Metallic zinc—often called *spelter* in commerce—has numerous uses. For instance, zinc plates are very extensively used for roofing. Iron is frequently coated with zinc to prevent rusting; it is then known as *galvanized iron*. Further, zinc is a constituent of many alloys, e.g. brass (§ 242).

269. **Zinc oxide,** ZnO, is usually prepared by igniting the basic carbonate. On being heated it turns yellow; on cooling, the original white color returns. It is employed as a pigment under the name *zinc white*, or *Chinese white*.

Zinc hydroxide, $Zn(OH)_2$, is precipitated by alkalies from the solution of a zinc salt as a white gelatinous mass, soluble in the alkalies as well as ammonia; however, the reason is different in the two cases. In the presence of alkalies zinc hydroxide behaves as a weak acid; it forms ZnO_2'' anions and the cations $2H^{\cdot}$, which yield a salt $Zn(OK)_2$ with the alkali in the ordinary way (§ 66). When treated with ammonia, however, a complex zinc-ammonia ion is formed, which is soluble.

Zinc chloride, $ZnCl_2$, can be obtained by heating zinc in a current of chlorine or by dissolving zinc in hydrochloric acid and evaporating the solution. In the latter case some oxychloride is formed, however. Zinc chloride melts on heating and distils at 680°. It is very hygroscopic and is often used for splitting off water from organic compounds. On adding zinc oxide to a concentrated zinc chloride solution a soft mass is obtained, which soon becomes hard because of the formation of the basic chloride $Zn<^{OH}_{Cl}$. Ammonia unites with zinc chloride to form various compounds.

Zinc sulphate, $ZnSO_4 \cdot 7H_2O$, crystallizes in well-developed crystals, which are isomorphous with the analogous compounds $MgSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, etc. It is prepared commercially by carefully roasting zinc blende.

Zinc sulphide, ZnS, is completely precipitated by hydrogen sulphide from solutions of its salts to which sodium acetate has been added to neutralize the acid set free from the zinc salt. In the absence of sodium acetate it is still partially precipitated, even from solutions of the neutral salts of strong acids.

This is not the case with the salts of the other metals belonging to the same analytical group as zinc, e.g. with the ferrous and manganese salts. The difference is due to the greater insolubility of zinc sulphide. When hydrogen sulphide is passed into a zinc solution, which contains of course Zn-ions and acid anions, H_2S-molecules and H- and S-ions are introduced into the liquid so that we have side by side the ions:

$$Zn^{\cdot\cdot} + SO_4'' + 2H^{\cdot} + S''.$$

Especially if the zinc solution is concentrated, the solubility product of the Zn- and S-ions is soon reached, so that ZnS must be deposited. This action, however, will soon reach a limit, on account of the H-ions, which stay in the solution and almost completely suppress the ionization of the hydrogen sulphide molecules still present. By the addition of an excess of sodium acetate, however, these free H-ions are enabled to combine with the acetic anions, and this combination will be almost complete if an excess of the latter ions is present. The concentration of the H-ions thus becomes so slight that the zinc sulphide must all be deposited. If, however, the solubility product of the sulphide is not so small, as in the case of ferrous and manganese sulphides, the slight ionization of the hydrogen sulphide renders it impossible for the solubility product to be reached, or, in other words, the sulphides will not be precipitated. Zinc, by reason of the solubility of its sulphide, thus assumes an intermediate position between the metals that are not precipitated by hydrogen sulphide and those that are. The solubility of the sulphides must decrease in the series FeS . . . ZnS . . . CuS. There is no sharp difference between these two analytical groups but rather a gradual transition from one to the other.

CADMIUM.

270. Cadmium is very frequently found in zinc ores. Being more volatile than zinc, it distils over first in the extraction of such ores. It is obtained pure by repeated distillation or by conversion into the sulphide, which is insoluble in dilute acids and can therefore be easily separated from zinc sulphide.

Cadmium is a white, rather soft metal; sp. g., 8.6; m.-pt., 315°; b.-pt., 778°. It is unaffected by the air but burns on heating, forming a brown cloud of oxide. It is difficultly soluble in dilute hydrochloric and sulphuric acids, but readily soluble in dilute nitric acid. The cadmium molecule in the gaseous state contains only one atom.

Cadimum oxide, CdO, is obtained as stated above and also by heating the carbonate or hydroxide. It is an amorphous brown powder. **Cadmium hydroxide,** $Cd(OH)_2$, is insoluble in caustic potash or caustic soda but soluble in ammonia, on account of the formation of a complex ion. **Cadmium chloride,** $CdCl_2$, crystallizes with two molecules of water and, unlike zinc chloride, can be dried without decomposition. **Cadmium sulphide,** CdS, is characterized by a bright yellow color (it is used as a pigment). It is insoluble in acids. The **sulphate,** $CdSO_4$, usually crystallizes out of its aqueous solution as $3CdSO_4 \cdot 8H_2O$. There is also a salt $CdSO_4 \cdot 7H_2O$, which is analogous in composition to the sulphates of magnesium, zinc, iron, etc.

MERCURY (Quicksilver).

271. Mercury is the only metal that is liquid under ordinary conditions. It occurs in nature in *cinnabar*, HgS, and also *native.* The chief localities are Almaden in Spain, Idria in Illyria, Mexico, Peru, California, China and Japan. To obtain mercury from cinnabar the latter is roasted in furnaces, sulphur dioxide and mercury being formed. The mercury vapor is condensed either in large chambers or in peculiarly shaped earthen retorts, or pipes, called *aludels.* It is brought on the market in 75-lb. iron flasks.

The commercial product is not pure, containing more or less of other metals in solution (e.g. lead, copper, etc.). Such impurities can be readily detected by the fact that they make the mercury adhere to a glass vessel. A suitable process of purification consists in letting it fall in fine drops through a long column of nitric acid (sp. g., 1.1), as in Fig. 69 The foreign metals are thus completely dissolved, while almost no mercury is lost by solution, because these foreign metals precipitate mercury from its salt solutions. After being washed with water the metal is dried and, if absolute purity is desired, it is then distilled *in vacuo.* But a vacuum distillation of itself is insufficient, for some lead goes over with it.

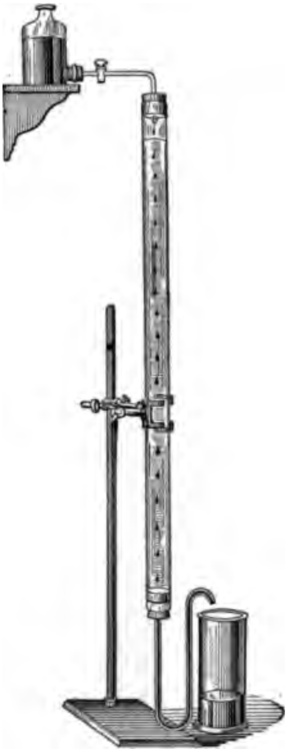


FIG. 69.—PURIFICATION OF MERCURY.

Physical Properties.—Mercury solidifies at − 39.4° and boils at 360°. Even at ordinary temperatures it is somewhat volatile, especially under reduced pressure; when gold leaf is suspended in a bottle over mercury, for instance, it eventually becomes white. The metal has a specific gravity of 13.595 at 0°. The vapor density is 99.36 for $H=1$; hence the molecule weighs 198.72. This number also represents the atomic weight, as has been found from molecular weight determinations of many volatile mercury compounds.

Amalgams.—Many metals have the property of dissolving in mercury or forming compounds with it. These metal solutions or compounds are called "amalgams." Besides by the direct contact of the two metals they can sometimes also be obtained by allowing mercury to act on the solutions of metal salts, e.g. silver amalgam can thus be prepared. Some metals, such as tin, dissolve in mercury with heat absorption; others like potassium and sodium with great heat evolution and vigorous action. If a great excess of mercury is used, the amalgams are liquid, otherwise solid. Sodium amalgam is exceedingly firm when it contains more than three per cent. of sodium.

Opinions have been divided as to whether amalgams, and metallic alloys in general, are mixtures or compounds. In order to solve the question a study has been made of the freezing-point curves (cf. § 237) of different pairs of metals. Additional information, often of a decisive nature, has been afforded by the microscopical examination of the surface of the alloy after having been etched with dilute acid and polished, the individual crystals being generally distinguishable in this way. As a result of these investigations it has been found that the freezing-point curves for pairs of metals

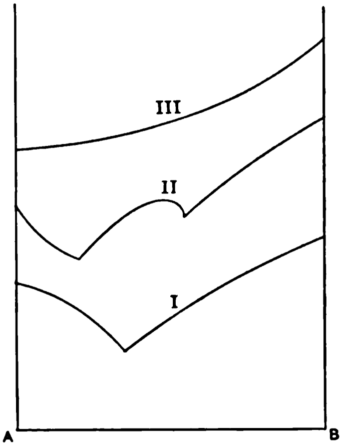


FIG. 70.—TYPICAL FREEZING-POINT CURVES OF PAIRS OF METALS.

(binary alloys) may be of three different types (Fig. 70). In some cases there is no association of the metals and the curve (I) takes the same form as the freezing-point curve of a salt solution, having a eutectic point. In others a compound may be formed (II), in which two eutectic points are observed, one for each of the components with the compound. The compound has the composition corresponding to the abscissa for the maximum of the curve between the eutectic points, the freezing-point of the pure compound being lowered by the addition of one of the components, just as is the freezing-point of a pure component by the addition of the other component. In still other typical cases the components may form mixed crystals, or solid solutions (§ 260). The form of the freezing-point curve (III) is very instructive in this case. When mixed crystals can be formed in all proportions the curve has no eutectic point; every liquid phase gives crystals of a definite composition corresponding to the composition of the liquid phase. The freezing-point curve is uninterrupted in its course.

In addition to the above three types we may have various combinations of them. Investigations of the above sort have shown that amalgams of potassium and sodium form compounds, such as Hg_4Na and Hg_7Na. In the amalgams of zinc there are neither compounds nor mixed crystals. Mixed crystals are formed in the amalgams of tin, lead, and cadmium.

The study of the solid products of the cooling of molten metallic mixtures seems at first somewhat complicated, because we may have not only the solids that result from the slow cooling in accordance with the freezing-point curves, but we may also have solid metallic mixtures formed by the sudden chilling of a hot mixture. This possibility is rather advantageous, however, since we are thus enabled to fix for study at room temperature the relationships prevailing at a higher temperature.

Chemical Properties.—At ordinary temperatures the metal is not affected by the air; at higher temperatures it takes up oxygen to form the oxide HgO, which, however, splits up again into its elements on further heating. Dilute hydrochloric and sulphuric acids do not attack it at ordinary temperatures and dilute nitric acid acts only in the presence of nitrogen dioxide (see § 127). Mercury unites instantaneously with the halogens and sulphur.

Mercury forms two sets of salts, *ous* and *ic*, the former being derived from *mercurous oxide*, Hg_2O, and the latter from *mercuric oxide*, HgO.

Mercurous Compounds.

272. Mercurous oxide, Hg_2O, is dark brown. It is precipitated from the solution of a mercurous salt by caustic soda. It decomposes at as low a temperature as 100° or in the light, yielding mercuric oxide, HgO, and mercury.

Mercurous chloride, Hg_2Cl_2, *calomel,* can be prepared in the wet way by precipitating a dissolved mercurous compound with a chloride, or in the dry way by subliming a mixture of mercuric chloride and mercury. It is a white powder, insoluble in water, but turns dark in the light on account of the separation of metallic mercury. Ammonia blackens it by forming a mixture of mercuric ammonium chloride, NH_2HgCl, and finely divided mercury:

$$2HgCl + 2NH_3 = H_2NHgCl + NH_4Cl + Hg.$$

Calomel is frequently used as a medicament.

The vapor density of calomel has been found to be 117.6 ($H = 1$), which corresponds to the molecular formula HgCl. When calomel evaporates, however, a dissociation into $HgCl_2$ and Hg occurs; these products unite again on cooling, but they can be previously separated by diffusion. It is for the above reason that the vapor density was found to be half the amount calculated for Hg_2Cl_2; hence the correct formula of calomel is Hg_2Cl_2.

Here also BAKER noted the influence of traces of water (*cf.* pp. 331, 332). According to his investigations thoroughly dried mercurous chloride does not dissociate on volatilizing and gives a vapor density which corresponds to the formula Hg_2Cl_2.

Mercurous bromide and **iodide** are even less soluble than the chloride. The solubility decreases, as in the case of silver, with an increase in the atomic weight of the halogen.

Mercurous nitrate, $HgNO_3$, is formed when cold dilute nitric acid acts on an excess of mercury. It is hydrolyzed by water, a yellow basic salt $Hg_2{<}{\substack{OH \\ NO_3}}$ being deposited. It therefore dissolves without decomposition only in dilute nitric acid. The mercurous ion is evidently only very feebly basic. A solution of mercurous nitrate is slowly oxidized by the oxygen of the air to the mercuric salt, but the addition of a little mercury reconverts it into the lower form.

Mercuric Compounds.

273. **Mercuric oxide,** HgO, is red and crystallized when prepared by heating mercury or mercury nitrate, but yellow and amorphous when precipitated from solutions by a hydroxide of

potassium or sodium. The difference between these forms seems to be due only to a difference in the coarseness of their grains. Mercuric oxide turns black on heating and red on cooling.

Mercuric chloride, $HgCl_2$, *corrosive sublimate,* is manufactured on a large scale by heating a mixture of common salt and mercuric sulphate; it sublimes over, whence its name. At room temperature 1 part $HgCl_2$ dissolves in 15 parts H_2O. It is more soluble in alcohol. The acid reaction of its aqueous solution indicates hydrolytic dissociation; if sodium chloride or potassium chloride is added to the liquid, the reaction becomes neutral because of the formation of a double salt $HgCl_2 \cdot KCl \cdot H_2O$. This is more soluble in water than sublimate itself.

Mercuric iodide, HgI_2, is yellow when it is first precipitated from the solution of a mercuric salt by potassium iodide, but it soon becomes red. If this modification is heated, it passes over into a yellow form at 150°, the original red color returning on cooling, however. There is evidently a transition point here.

Mercuric iodide dissolves readily in potassium iodide solution. NESSLER's solution, a very valuable reagent in testing for ammonia, is made by mixing the above mercuric iodide solution with caustic potash. It should be noted, however, that many organic nitrogen compounds give much the same coloration as ammonia with NESSLER's solution.

Mercuric cyanide, $Hg(CN)_2$, is obtained by boiling Prussian blue with mercuric oxide. It crystallizes in fine large colorless crystals.

274. The mercuric halides, in contrast to the other salts of the mercuric ion, are only slightly ionized in aqueous solution. For this reason they exhibit some peculiar reactions. On mixing a mercuric solution with one of a chloride, for instance, considerable heat is given off because undissociated $HgCl_2$ molecules are formed, while the mixture of solutions ordinarily obeys the law of thermoneutrality (§ 238, 2).—Again, if mercuric oxide is shaken with a solution of chloride, bromide, or iodide of potassium, the liquid becomes strongly alkaline because of the liberation of potassium hydroxide. This is due partly to the slight ionization of the mercury halides and partly to the combination of the latter with the excess of alkali halide to form very stable alkali

mercuric halides. The stability of these complex compounds increases with rising atomic weight of the halogen.—The same cause explains the reverse fact, viz., that the halogen compounds of mercury are only with difficulty decomposed by alkalies. In order to precipitate all the mercury from mercuric chloride a large excess of potassium hydroxide must be employed; mercuric iodide and mercuric cyanide cannot be decomposed by potassium hydroxide alone. Mercuric cyanide is so little ionized that its conductivity can hardly be measured; hence it does not give any of the ordinary mercury reactions, except the formation of the sulphide (since the latter is so very insoluble). This cyanide can be regarded as a type of compounds rendered inactive because of non-ionization.

This low ionization also explains the formation of mercuric cyanide according to the method mentioned above. When mercuric ions and cyanide ions are brought together, even in extremely dilute solution, they must unite to form $Hg(CN)_2$ molecules. The union of these ions necessitates the sending of more of them into solution by the mercuric oxide and Prussian blue, and so the process goes on until the formation of mercuric cyanide and ferric oxide, Fe_2O_3, is complete.

The mercuric halides (especially corrosive sublimate) are very strong antiseptics. It is an interesting fact that in this respect also, they become more effective as their ionization increases. The chloride is a more powerful antiseptic than the cyanide. The addition of metal chlorides diminishes the ionization of sublimate and at the same time reduces its disinfecting ability.

The reason why the mercuric chloride for use in sublimate tablets is nevertheless mixed with an excess of common salt is partly that the sublimate is thus dissolved more rapidly and also because such solutions keep longer than those of the pure sublimate, especially when prepared with well-water.

Mercuric nitrate, $Hg(NO_3)_2$, forms basic salts very readily; on diluting its solution in nitric acid with water there is deposited a compound $Hg(NO_3)_2 \cdot 2HgO \cdot H_2O$, which is converted into pure mercuric oxide by boiling with water. This shows that the bivalent mercuric ion, also is very feebly basic.

Mercuric sulphate is not soluble in water but is converted by the latter into a basic salt. In the presence of much water the yellow compound, $HgSO_4 \cdot 2HgO$, is formed. With the sulphates of the alkalies it forms double salts, e.g. $HgSO_4 \cdot K_2SO_4 \cdot 6H_2O$, which are isomorphous with the corresponding double salts of magnesium (§ 255), iron, etc.

Mercuric sulphide, HgS, is black when precipitated from solution; on being heated in the absence of air it sublimes in dark-red crystals, which are similar to natural cinnabar and are used as a pigment (*vermilion*).

SUMMARY OF THE GROUP.

275. Here again a gradual change in the physical properties is to be seen as the atomic weight rises. The following small table presents a few of the constants:

	Be	Mg	Zn	Cd	Hg
Atomic weight........	9.1	24.36	65.4	112.4	200.0
Specific gravity.......	1.64	1.75	6.9	8.6	13.6
Melting-point........	>900°	>700°	412°	320°	−39.4°
Boiling-point..........	....	>Zn	920°	778°	360°
Atoms in molecule....	....	....	1	1	1

In respect to chemical properties it should be noted that all of these elements are bivalent, except that mercury can be considered as univalent in its ous-compounds. Their sulphates unite with those of the alkalies to form double salts of the same type, $RSO_4 \cdot R_2'SO_4 \cdot 6H_2O$ ($R' = K, Na, NH_4$); the beryllium double salt alone crystallizes with $3H_2O$. The hydroxides of this group are soluble in ammonia with the formation of complex ions, or else they yield insoluble metal-ammonia compounds (Hg).

The neutral salts have a tendency to go over into basic salts. This is especially marked in mercury; in the case of cadmium it is, strange to say, very weak.

With the halogen compounds of the three related metals Zn, Cd and Hg the electrolytic dissociation is small; it decreases as the atomic weight of the metal rises and is very slight in the case of mercury.

ELECTROCHEMISTRY.

276. As early as the beginning of the nineteenth century, when Davy isolated the alkali metals by means of the electric current (§§ 223 and 227), there was known to be an intimate relation between electrical and chemical phenomena. Berzelius even went so far as to suppose that affinity could be perfectly explained by assuming that the atoms are electrically charged and that these charges are the attractive or repellent forces. The galvanic element has been for a long time a familiar means of converting chemical energy into electrical energy. However, it was not until 1889 that a theoretical explanation of the connection between chemical and electrical phenomena was offered; this explanation by Nernst is not only a very satisfactory one, but it also affords an insight into numerous chemical phenomena. The key to the explanation is the concept of "electrolytic solution tension," which has already been referred to in a few instances (§§ 203 and 268).

When a metal comes in contact with the aqueous solution of one of its salts a *difference in potential* develops between the two. This phenomenon is explained by Nernst as follows: Just as a liquid continues to evaporate at its surface until the pressure of the vapor becomes equal to the vapor tension of the liquid, so a salt must continue to dissolve in water (evaporation and solution being analogous processes) until the osmotic pressure of its solution balances the solution tension of the salt. Now, according to Nernst, every metal also has a certain tendency, dependent only on its chemical nature, to force its atoms into solution as ions. This force, called the **electrolytic solution tension,** comes into action when the metal is immersed in an electrolyte and its strength is the less, the more cations of the metal are already in the solution. The amount of cations sent into the solution is very small, as experiment shows,—so much so that it cannot be determined by the usual chemical means. The cause of this is not that the solution tension is low,—on the contrary, the latter is often very large—but that an equilibrium is very soon reached, because, notwithstanding the low concentration of the ions, they carry a very high electrical charge and the negatively charged metal soon attracts its positive ions in the solution with such force that just as many ions are precipitated on the metal as are sent out into the solution. If P represents the solution tension of a metal and p the osmotic pressure of the cations in the solution, there are three possibilities to be distinguished:

(1) $P>p$. The metal then behaves like a salt in contact with its own unsaturated solution. It forces cations into the solution of the electrolyte, so that the solution becomes positively charged and the metal has to take on a negative charge. An equilibrium is soon established. However, if the free positive and negative electricities acquired by the electrolyte and the metal are conducted away by a connecting wire the metal will again send cations into the solution, and this action will continue till p reaches the value of P.

(2) $P=p$. There can be no potential difference.

(3) $P<p$. In this case the metal corresponds to a salt introduced into its supersaturated solution. Cations are now deposited on the metal and charge it positively, the electrolyte becoming negative. Here also a state of equilibrium must soon arise since the negatively charged electrolyte tends in turn to draw the positive metal ions back into solution.

The relation between the potential difference E and the magnitudes P and p, is expressed by NERNST with the equation:

$$E=\frac{RT}{n}\log_e\frac{P}{p}, \quad \ldots\ldots\ldots \quad (1)$$

in which R is the gas constant, T the absolute temperature, n the valence of the metal ions and $\log_e$ the natural logarithm

If for R in this equation the value is substituted which was calculated in § 34, E is not obtained in volts, since electrical magnitudes are measured in other units than those there employed. In this case we must introduce for R the value 0.860×10^{-4}. If BRIGGS' logarithms are to be used, the modulus 2.3025 must also be included. The value of E in volts then becomes:

$$E=\frac{0.860\times10^{-4}\times2.3025T\log\frac{P}{p}}{n},$$

or

$$E=10^{-4}\cdot\frac{2T}{n}\log\frac{P}{p}.$$

From this equation it is seen that E increases arithmetically when p decreases geometrically. For example, if the ionic concentration is reduced to one-tenth, E only increases by $\frac{2T}{n} \times 10^{-4}$ volt. It is thus seen that the potential difference is not much affected by changes in the concentration of the electrolyte, even though they be quite large.

On bringing together two different metals and their salt solutions an element, or cell, of the DANIELL type is obtained (copper in copper sulphate and zinc in zinc sulphate, the two pairs separated by a porous partition). The electromotive force of such a cell is found from the difference of the two values of E, i.e.

$$E = \frac{RT}{n}\left(\log_e \frac{P_1}{p_1} - \log_e \frac{P_2}{p_2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when both metals have the valence n.

In such a cell with closed circuit there are differences of potential not only between metal and solution but also between the two liquids and between the two metals. Experience has shown, however, that both of the latter are very small in comparison to the former, so that they may be disregarded.

Leaving the solution tensions P_1 and P_2 out of consideration, E therefore depends on the values of the osmotic pressure p_1 and p_2 of the metal-ions. If p_2 can be made extremely small, so that $\log_e \frac{P_1}{p_1} < \log_e \frac{P_2}{p_2}$, E becomes negative, i.e. the current must alter its direction. This can be demonstrated as follows:

In a DANIELL cell, in which the osmotic pressure of the zinc ions (p_1) is seldom very different from that of the copper ions (p_2), the current goes from the copper through the connecting wire to the zinc, for the solution tension (P_1) of the zinc is much larger than that (P_2) of the copper (see below). Now the concentration of the copper ions can be made several powers of ten smaller by adding potassium cyanide to the copper sulphate solution, for by this means the very slightly ionized complex $(Cu_2Cy_4)''$ is formed (§ 243). This addition actually reverses the direction of the current. Neither the precipitation of the copper by potassium hydroxide nor the precipitation by ammonium sulphide reduces the concentration of the copper ions enough to produce this effect.

Since equation (2) can also be written

$$E=\frac{RT}{n}\left(\log_e\frac{P_1}{P_2}-\log_e\frac{p_1}{p_2}\right),$$

and, when $p_2=p_1$, the last expression becomes zero, it is apparent that the electromotive force of a Daniell cell is mainly determined by the ratio of the solution tensions of the metals. *A galvanic cell can be regarded as a machine driven by the electrolytic solution tensions of the metals.*

The introduction of this conception of solution tension and the ideas connected with it has led to an altogether clearer understanding of the chemical processes of galvanic cells, as well as of the way in which the current is generated in them.

Galvanic cells may be divided into two classes, *reversible* and *non-reversible*. The Daniell belongs to the first class. It produces a current because the solution tension of the zinc exceeds that of the copper. The zinc sends its positively charged ions into the sulphate solution and itself becomes negative. On the other hand, the copper ions, on passing over into atoms and precipitating themselves on the copper plate, transfer their positive charges to the latter, which thus becomes the positive pole. Chemically the process amounts to the simultaneous solution of zinc and precipitation of copper:

$CuSO_4+Zn=Cu+ZnSO_4$, or in ions: $Cu^{\cdot\cdot}+Zn=Cu+Zn^{\cdot\cdot}$.

If a current is sent through the Daniell cell in the opposite direction, ions will enter into solution at the copper plate because the latter acquires a positive charge, and the zinc ions will be forced to deposit themselves on the zinc, for the reverse current charges the zinc negatively so that it attracts the zinc ions. It is therefore possible by passing a reverse current through the cell to restore it to its original condition,—hence the term "reversible."

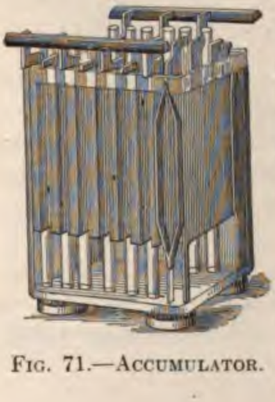


Fig. 71.—Accumulator.

One of the most important styles of reversible batteries is the **accumulator,** or storage-battery (Fig. **71**). This consists of a glass jar in which lead plates are suspended so that they dip into dilute sulphuric acid. These plates are coated alternately with lead peroxide (positive) and lead sulphate (negative). The positive plates are all connected with each other, as are also the negative ones. (From a large number of such cells a battery is constructed by connecting the positive pole of each cell with the negative pole of the adjoining one.) If a current is passed through the system so that it enters at the lead peroxide plate and goes through the sulphuric acid to the other plate, lead peroxide collects on the positive plate, while on the other, the cathode plate, the lead sulphate is converted into spongy lead. By this process the accumulator is charged. Thereupon, if the poles are connected (by a wire), the opposite process goes on; the lead peroxide is reduced at the one plate and the spongy lead is converted into lead sulphate at the other. During the discharge the peroxide plate is again positive, the lead plate negative. The chemical process in the accumulator cell is therefore expressed by

$$PbO_2+Pb+2H_2SO_4 \rightleftarrows 2PbSO_4+2H_2O.$$

The generation of the current has been explained in various ways. One is as follows: The lead peroxide on the anode plate has a certain solution tension, and hence goes into solution as negatively charged PbO_2'' ions. Thereby it of course imparts to the plate istelf a numerically equivalent positive charge. These bivalent PbO_2'' ions encounter positively charged $Pb^{\cdot\cdot}$ ions at the cathode plate, which are being sent by it into the solution; the cathode plate charges itself negatively at the same time. The two sorts of ions now combine to form electrically neutral PbO molecules, which yield lead sulphate with the sulphuric acid present:

$$PbO_2''+Pb^{\cdot\cdot}=2PbO;\ 2PbO+2H_2SO_4=2PbSO_4+2H_2O.$$

Among the non-reversible cells are the BUNSEN and the LECLANCHÉ. A reverse current does not restore these to their original condition and their electromotive forces E cannot be calculated by the above formula; nevertheless the general principles of the pressure theory can be applied to explain the production of the galvanic current in these cells.

The arrangement of the BUNSEN cell—an amalgamated zinc plate dipped in sulphuric acid and a carbon cylinder in nitric or chromic acid—is well known. From an electrochemical standpoint the generation of hydrogen from zinc and sulphuric acid amounts to a transfer of the charges of the hydrogen ions of the dilute acid to the zinc atoms and an escape of hydrogen in the form of discharged molecules. In the BUNSEN cell, however, most of the hydrogen ions find an opportunity to give up their positive charges to the carbon cylinder and exercise a reducing action on the nitric or chromic acid. On the other hand the zinc plate sends positively charged zinc ions into the solution to the same extent as hydrogen ions disappear, the zinc plate itself acquiring a negative charge.

The LECLANCHÉ cell consists of a zinc bar in concentrated ammonium chloride solution and a porous earthenware cylinder immersed in the same solution and containing some manganese peroxide and a stick of carbon for conducting off the current. Here again the zinc goes into solution:

$$Zn + 2NH_4Cl = ZnCl_2 \cdot 2NH_3 + H_2.$$

The hydrogen ions discharge themselves at the carbon and reduce the peroxide. In this case also the carbon is the positive, the zinc the negative, pole.

277. Just as in galvanic cells chemical energy is transformed into electrical energy, so reactions between ions in general can produce an electric current if the conditions are suitable. A few examples of this may be cited.

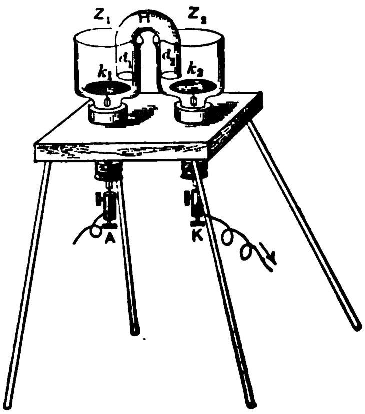


FIG. 72.—LÜPKE CELL.

For these experiments a cell devised by LÜPKE is very satisfactory (Fig. 72). It consists of two glass vessels Z_1 and Z_2, to the bottoms of which the platinum electrodes k_1 and k_2 are attached. The vessels are connected by means of the wide siphon H. The wires A and K lead to a galvanoscope. To show that electrical energy can be obtained by the oxidation of the stannous to the stannic chloride an acidulated stannous chloride solution (11.2 : 100) is introduced into Z_1

and an acidulated normal sodium chloride solution into Z_2; the siphon also is filled with the latter solution. As soon as a few drops of chlorine-water or a solution of auric or mercuric chloride are allowed to fall from a pipette upon the electrode (k_2) in the salt solution, the galvanoscope indicates a current in the wire circuit from K to A. Now, in order that the bivalent ion $Sn^{\cdot\cdot}$ may become quadrivalent ($Sn^{\cdot\cdot\cdot\cdot}$) it must acquire two more positive charges and this requires the addition of two chlorine ions. These are at once supplied by the mercuric or auric chloride. The metallic ions ($Hg^{\cdot\cdot}$ or $Au^{\cdot\cdot\cdot}$) are deposited on k_2 and impart to the latter a positive charge, which, if conducted by means of the wire circuit K, is at the disposal of the $Sn^{\cdot\cdot}$ ions. If free chlorine is added, it splits up into ions, as a result of which positive electricity is imparted to k_2 and this flows through the wire circuit back to k_1 and raises the potential of the $Sn^{\cdot\cdot}$ ions.

The precipitation of silver chloride, according to the equation

$$NaCl + AgNO_3 = AgCl + NaNO_3,$$

can be made to produce an electromotive effect by laying a polished piece of sheet silver on each platinum electrode of the above apparatus and filling Z_1 with sodium chloride solution and Z_2, as well as the siphon, with an equimolecular sodium nitrate solution. As soon as a crystal of silver nitrate is placed on the electrode k_2 (in the nitrate solution) a current is detected. Previous to the introduction of the silver nitrate crystal both pieces of silver, because of their solution tensions, drive equal amounts of silver ions into solution, but equilibrium is very soon reached (§ 276). The crystal, however, has caused the formation, around the electrode k_2, of a concentrated silver solution, whose osmotic pressure far exceeds the solution tension of the metal. As a result silver ions are thereupon deposited on k_2, and this electrode becomes positively charged; this charge passes through the wire circuit to k_1. The result of this is the sending of more silver ions into the salt solution around k_1, but their concentration very soon becomes so great that the solubility product of silver chloride is exceeded and the latter is precipitated on the silver plate in Z_1.

The fact that electrical energy can be obtained by the neutralization of sulphuric acid is capable of demonstration with the same apparatus. To this end a $\frac{1}{2}$-normal sulphuric acid is introduced into Z_2 and a $\frac{1}{2}$-normal potassium sulphate solution into Z_1 and the siphon. If a large piece of palladium foil (about 4 sq. cm.) that has been saturated electrolytically with hydrogen is placed on the platinum disk of the electrode k_1 and touched for a few moments with a stick of caustic potash, bubbles of hydrogen will rise from the platinum plate of the other electrode k_2 and the needle of the galvanoscope will indicate the passage of a powerful current outward from k_2. The hydrogen of the palladium foil sends positive ions into the solution, which, however, forthwith unite with the OH-ions of the potassium hydroxide to form neutral water. By the emission of these positive ions k_1 acquires a negative potential, which flows out through the external circuit to k_2. The hydrogen ions of the sulphuric acid surrounding this electrode are thus afforded an opportunity of discharging themselves against this negative charge so that hydrogen is given off in the free state.

In the combination of chlorine (or oxygen) and hydrogen chemical energy can also be transformed into electricity. To accomplish this, two tubes sealed at the top and fitted there with platinum electrodes, reaching almost to the open end of the tubes, are filled, one with hydrogen and the other with chlorine (oxygen) and inverted in dilute sulphuric acid. On connecting the electrodes by a wire a strong current traverses the circuit. The gases absorbed in the platinum electrodes drive their ions into the surrounding liquid, making the H-electrode negative and the Cl(O)-electrode positive. The ions of hydrogen and chlorine dissolve in the dilute sulphuric acid, however. This apparatus is called GROVE's gas battery and was known long before a satisfactory explanation of it could be given.

In conclusion we may cite a case where a current is obtained by the partial discharge of ions. If a piece of sheet iron is introduced into a sodium chloride solution from above and a similar piece of platinum is laid on the bottom of the vessel, a galvanoscope inserted in the circuit between the metals shows no current; but if the platinum at the bottom is surrounded with ferric ions by dropping in a little solid ferric chloride, a current is immediately formed. The ferric ions send through the wire one-third of their (positive) charge to the iron plate and this enables the iron to keep on sending ferrous ions into the liquid until all the ferric chloride added has been converted into ferrous chloride.

It is characteristic of all these various cells that *the reacting substances are apart from each other*. In the oxidation of stannous chloride by mercuric chloride the latter was not put in the vessel with the stannous chloride but in the other vessel; in the precipitation of silver chloride the silver nitrate was not put with the sodium chloride solution but with the sodium nitrate solution, and so on. The reaction took place only because one sort of ions transferred their electrification wholly or in part through the wire circuit to the other electrode, where it either converted atoms into ions or raised existing ions to a higher potential or, possibly, changed ions of opposite potential sign to neutral atoms.

Since we know that chemical reactions can under suitable conditions produce an electric current, we can, conversely, regard the existence of such a current as an indication of the occurrence of a chemical reaction. COHEN has made use of this fact in determining electrically the *transition points* of hydrous salts and other systems. Let us take, for example, a salt which loses its water of crystallization at a definite temperature, e.g. Glauber's salt, $Na_2SO_4 \cdot 10H_2O$; this has a transition point at about 33°, where the anhydrous salt becomes capable of permanent existence. Now it is possible for the anhydrous salt to remain in contact with its saturated solution in an unstable condition after the system has been cooled a few degrees below 33°; the reverse is also true of the hydrous salt. Since these solutions are in contact with different solid phases (one with $Na_2SO_4 \cdot 10H_2O$ and the other with Na_2SO_4) they do not have the same concentration; at the transition point, however, these concentrations become equal, for since both solid phases are in contact with the solution in each case, the solubility becomes the same. In his electrical method COHEN uses the difference in concentration of the solutions which are saturated in respect to the two solid phases to form a galvanic cell. This can be done as follows: In the bottom of each of the cylinders *A* and *B* (Fig. 73) there is a little mercury. A platinum wire is fused into each cylinder and the two are connected by means of a metallic wire. On top of the mercury is some insoluble mercurous sulphate; above this in *A* is a paste of $Na_2SO_4 \cdot 10H_2O$ and water, in *B* is a similar mixture of water and Na_2SO_4. Below the transition point the solution in *B* is in the unstable condition and more concentrated than that in *A*, which is stable. The result is that sodium ions diffuse through the siphon from the concentrated to the dilute solution, while at the same time an equivalent amount of SO_4-ions in *B* combines with part of the mercury to form mercurous sulphate, the negative charge of the sulphate ions being transferred to the remaining mercury. Thus an electric current is produced which passes through the wire circuit from the dilute to the concentrated solution. Its direction and intensity can be determined by inserting a galvanometer in the circuit.

Now, suppose that the whole apparatus is gradually warmed; the concentrations in *A* and *B* will approach each other as the temperature nears the transition point and at this point they will become equal. The intensity of the current will therefore decrease steadily till the transition point is reached, when it is zero. If the temperature is raised still higher the solution in *A* will become unstable and more concentrated than that in *B*, which latter will then be the stable solution; as a result the direction of the current will be reversed. In this way it is possible to determine the transition point very accurately.

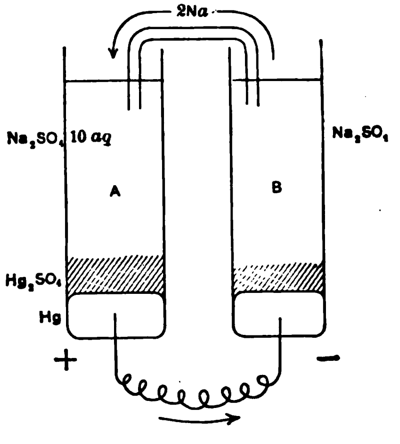


FIG. 73.

278. As was remarked in § 276, the electromotive force which can be obtained from chemical reactions depends in large measure on the solution tensions of the metals. A knowledge of the latter

is therefore of very great importance. It can be acquired with the aid of the equation previously given:

$$E=10^{-4}\cdot\frac{2T}{n}\log\frac{P}{p}.$$

E, the difference of potential between a metal and the aqueous solution of one of its salts can be measured. All the other quantities of this equation are known with the exception of P, which can therefore be calculated, as is illustrated in the following example:

The potential difference between magnesium and the normal solution (½ mole per liter) of its sulphate was determined to be 1.22 volts. The equation thus becomes:

$$1.22=10^{-4}T\log\frac{P}{p},$$

since for magnesium $n=2$. p is the osmotic pressure of the Mg-ions. On the assumption that the salt is entirely split up into ions, p is 22.4 Atm., for, osmotic pressure being equal to gas pressure, 1 mole gas at 0° and 760 mm. occupies a volume of 22.4 liters (§ 34); hence, if the volume is a liter, the pressure becomes 22.4 Atm. Therefore, at 0° we have:

$$1.22=10^{-4}\times273(\log P-\log 22.4),$$

or $\log P=43.23$, whence we have, approximately,

$$P=10^{43}.$$

The following brief table indicates some of the results for different metals:

Metal.	Valence.	Solution Tension in Atmospheres.
Magnesium	2	10^{43}
Zinc	2	10^{18}
Aluminium	3	10^{13}
Cadmium	2	10^{7}
Iron	2	10^{3}
Nickel	2	10^{0}
Lead	2	10^{-3}
Hydrogen	1	10^{-4}
Copper	2	10^{-12}
Mercury	1	10^{-16}
Silver	1	$10^{\;15}$

The above figures show how enormously the solution tension differs in different substances. For magnesium and zinc it is many millions of atmospheres, for copper, mercury (ous) and silver extremely small fractions of an atmosphere. Despite the comparatively large errors in the above data, due to the difficulty of determining the potential difference between the metal and its salt solution, the order of the decimal expressing the value of *P* can be accepted as reliable in each instance.

Some of these *differences of potential between metals and their normal salt solutions* are as follows:

Metal.	Volt.
Mg	+1.22
Mn	+0.798
Zn	+0.439
Al	+0.22
Cd	+0.143
Fe	+0.063
Tl	+0.045
Co	−0.043
Ni	−0.049
Pb	−0.129
H	−0.277
Cu	−0.606
Hg	−1.027
Ag	−1.048

The algebraic sign of these differences of potential can be directly determined from the solution tensions. The electrolyte in which zinc is immersed must assume a positive potential and the metal itself a negative potential, because no zinc solution can be concentrated enough to hinder the emission of (positive) zinc ions by the metal. On the other hand, copper must become positive in respect to a copper solution, for even in the most dilute solutions the osmotic pressure of the copper ions is greater than the solution tension of the metal.

279. A knowledge of the electrochemical series of the metals in electrolytes is of great practical value. Wherever combinations of various metals, alloys, metallic crustations, etc., are exposed to atmospheric action there is an opportunity to form cells of short circuit. In general, the metal with the greatest solution tension goes into solution and the other remains intact. A piece of galvanized (zinc-plated) iron wire does not rust, even in those places where the plate has been worn off, as much as if it were not zinc-

plated. The reverse phenomenon, that tinned iron rusts faster than iron alone, is also due to galvanic causes. If our hypothesis is correct the atmospheric moisture adhering to the metal must act as an electrolyte with the combination tin-iron in such a way that iron becomes the dissolving (negative) electrode. Iron salts must therefore be formed and then transformed into rust by the loss of carbonic acid. The following experiment confirms this view. Rods of iron and tin are brought in contact by a wire which connects with a galvanometer. If the metals are dipped in water, into which air and carbonic acid are passed and to which is added a trace of sodium chloride (which always floats in the air and is washed down by the rain), the needle is deflected. The iron is found to be the anode, and in the course of an hour a thin yellow coating of rust is to be observed on it. Sheet iron is tinned, as is well known, to prevent it from rusting (§ 199). If the tin plating is scratched off at any place so as to expose the iron, the latter begins to rust very rapidly, more so even than if it were not tinned. Galvanized iron, however, does not show a trace of rust where the plating has been damaged.

280. An ion can only go out of solution when a force greater than the solution tension acts on it, just as electrically neutral molecules cannot crystallize out of a solution until its osmotic pressure exceeds that of the saturated solution. The removal of an ion can be brought about by the action of an electrical force. This is the real principle of electrolysis. The separation of an ion from a solution thus requires a definite electromotive force, which must be equivalent to $10^{-4}\frac{2T}{n}\log\frac{P}{p}$ (see above) and must therefore be stronger as the solution tension is greater and the osmotic pressure of the ions smaller. But since electrolysis takes place simultaneously at both the anode and the cathode, the total force E which is necessary for an electrolysis can be found by taking the sum of the forces necessary for the separation of the cation and the separation of the anion, thus:

$$E=E_1+E_2=2\times10^{-4}T\left(\frac{1}{n_1}\log\frac{P_1}{p_1}+\frac{1}{n_2}\log\frac{P_2}{p_2}\right).$$

Since it is always the case that various sorts of anions and cations are present together in a solution, electrolysis can thus take place when E has become large enough to separate out one of the varieties of cations and one of the varieties of anions present.

This is the basis of a method of utilizing various electromotive forces to effect an **electrolytic separation of metals.** It is not the current strength which is of primary importance to the electrolytic process (as was formerly supposed), but the difference of potential between the electrodes. A very successful example of this method is the separation of copper from zinc. With a current of low voltage it is possible to precipitate only the copper from a solution containing ions of both metals; if the electromotive force is increased, zinc also is separated.

In many cases the ions of the water are more easily separated out than those of the dissolved electrolyte. In the electrolysis of potassium hydroxide, for example, OH-ions are liberated at the anode (they are at once decomposed, however, into water and oxygen); at the cathode it is not potassium ions but hydrogen ions (in spite of their extremely small concentration) which are discharged, since the solution tension of hydrogen is much less than that of potassium.

281. The dissociation tensions E for various ions are given below. The figures are based on equivalent normal solutions.

The dissociation tension of hydrogen is fixed at zero in the table. Inasmuch as there is always an anode and a cathode. it is possible to subtract from all the values of E_1 an arbitrary but constant amount and add it to the values of E_2, without affecting $E(=E_1+E_2)$. The symbol O'' represents a secondary ionization product of the hydroxyl ion:

$$OH' = O'' + H^{\cdot},$$

the existence of which, according to Nernst, we are obliged to assume, although only to an extremely small degree.

Dissociation Tensions.

E_1 (Cations).	E_2 (Anions).
$Ag^{\cdot}$ −0.771	I' −0.520
$Cu^{\cdot\cdot}$ −0.329	Br' −0.993
$H^{\cdot}$ 0.0	O'' −1.23
$Pb^{\cdot\cdot}$ +0.148	Cl' −1.417
$Cd^{\cdot\cdot}$ +0.420	OH' −1.67
$Zn^{\cdot\cdot}$ 0.770	SO_4'' −1.9
	HSO_4' −2.6

These figures lead us to important results. In the first place they enable us to know at once the dissociation tension of any combination of ions. Zinc bromide, for instance, will require $0.993+0.770=1.763$ volts for its electrolysis; when the concentration of the ions is normal, the electrolysis of hydrochloric acid will require $1.417+0=1.417$ volts, and so on. It is also obvious that it must be easy to separate silver from copper electrolytically, since the difference of their dissociation tensions is almost 0.5 volt. It also appears theoretically possible to separate electrolytically iodine from bromine and bromine from chlorine.

The order of the metals in the above electrochemical series is the same as that in which one metal is precipitated from its solution by the succeeding ones. As soon as a trace of the dissolved metal is deposited on the other one, the two metals form with the liquid an element, which electrolyzes the surrounding solution. The formula

$$E=10^{-4}\frac{2T}{n}\log\frac{P}{p}$$

tells us, however, that the values of E depend not only on the solution tension but also on the osmotic pressure of the cations. Very decided changes in the concentration of the salt solution would make the order of the metals a different one. For instance, it would be possible to conceive a case in which lead would not be precipitated by cadmium.

The electrochemical series of the anions also brings out important relations. Bromine must quickly liberate iodine from iodide solutions and chlorine quickly liberate bromine from bromide solutions because of the marked difference in their dissociation tensions. We see, further, that chlorine must be able to generate oxygen in acid solutions, but not so with bromine or iodine. It is also known, however, that the generation of oxygen by chlorine proceeds with extreme slowness, in sharp contrast to the rapidity with which chlorine deprives bromine of its negative charge:

$$Cl_2+2Br'=Br_2+2Cl'.$$

This is not surprising in the light of the above considerations, for the chlorine, in order to enter the ionic condition, must make use of the ion O'', of which there is only an extremely small amount present. The hydroxyl ion OH′, which is present in relatively much larger amount and which after the loss of its negative charge would also yield a quantity of oxygen equal to that of the chlorine, holds its charge more than 0.3 volt firmer than the chlorine ion in acid solution.

The application of electrolysis to commercial processes is referred to in connection with the substances concerned (*cf.* §§ 223, 226, 242, 245, 248, and elsewhere).

BORON.

282. This element occurs in nature as *sassolite*, H_3BO_3, *boracite*, $Mg_7Cl_2B_{16}O_{30}$, *colemanite*, $Ca_2B_6O_{11}\cdot 5H_2O$, and *borax*, $Na_2B_4O_7\cdot 10H_2O$. It can be obtained in the elemental state by the reduction of boric anhydride, B_2O_3, or borax by means of magnesium powder. The product is extracted with boiling water and hydrochloric acid and then treated with hydrofluoric acid or fused with borax. After another treatment with boiling water the pure element is left as a chestnut-brown amorphous powder having a specific gravity of 2.45. It is insoluble in the ordinary solvents and does not melt even in the electric arc.

It dissolves in molten aluminium and crystallizes out on cooling in transparent, slightly colored crystals, having a lustre, refractive power and hardness not far below that of diamond. These crystals contain more or less aluminium and carbon as impurities. This crystallized modification is much less readily attacked by chemical agents than the amorphous variety.

Amorphous boron takes fire in fluorine and chlorine, uniting with them directly. When ignited in the air it burns to the oxide B_2O_3. At a very high temperature it combines with nitrogen to form boron nitride, BN. It reduces many compounds, such as CuO and PbO, and decomposes water at red-heat. Heating with nitric and sulphuric acids converts it into boric acid. It is also attacked by boiling caustic alkalies (like aluminium):

$$2B + 2KOH + 2H_2O = 2KBO_2 + 3H_2.$$

Boron hydride.—When boric anhydride is reduced with an excess of magnesium powder, *magnesium boride*, Mg_3B_2, is formed. The latter on being added to hydrochloric acid generates an ill-smelling gas consisting of hydrogen and a little boron hydride. This gas mixture burns with a green flame. By cooling with liquid air Ramsay and Hatfield obtained from it a gas B_3H_3; probably the mixture also contained BH_3.

Halogen Compounds.

Boron chloride, BCl_3, can be prepared by direct synthesis or by heating a mixture of boron trioxide and charcoal in a current of chlorine, that is, by the same process as that by which silicon chloride (§ 192) and aluminium chloride can be prepared. Boron chloride boils at 17°. Its vapor density indicates the above formula. Water breaks it up into hydrochloric and boric acids; it was with the aid of this reaction that the composition of the compound was determined.

Boron fluoride, BF_3, is formed, like silicon fluoride (§ 193), when the oxide is warmed with a mixture of calcium fluoride and sulphuric acid:

$$B_2O_3+3CaF_2+3H_2SO_4=2BF_3+3CaSO_4+3H_2O.$$

It is a gas, of which water dissolves 700–800 volumes. A solution of this concentration fumes in the air. On dilution boric acid separates out after some time; *hydrofluoboric acid,* $HF \cdot BF_3$, is left in the solution. This acid cannot be isolated in the free state but various salts of it are known. It thus displays a very close analogy to silicon fluoride.

Oxygen Compounds of Boron.

Boron oxide, B_2O_3, boric anhydride, is obtained as a vitreous mass by igniting boric acid. It is very hygroscopic and is reconverted by the absorbed water into boric acid. With hydrofluoric acid it forms boron fluoride. The oxide is volatile only at elevated temperatures.

283. Boric acid, H_3BO_3, is found in the volcanic districts of Tuscany, where jets of steam (the springs are called "fumaroles" and the jets proper "*soffioni*") containing a little boric acid issue from the earth. The steam is conducted into water, in which the boric acid is retained. When this liquid reaches a certain concentration, it is allowed to settle, whereupon it is piped off into a very long, flat leaden pan, which is warmed to about 50–60° by other *soffioni*. At this temperature the boric acid volatilizes but very little with steam and when the concentration has become great enough it crystallizes out. It is purified by converting it into borax, which is recrystallized and then decomposed by hydrochloric acid, setting free boric acid.

Considerable boric acid is also made by decomposing native borates with a strong mineral acid.

The volatility of boric acid with steam has for a long time been regarded as an especially interesting phenomenon, because the anhydride B_2O_3, into which it is readily converted at an elevated temperature, is only volatilized with extreme difficulty. The question therefore arises as to the particular compound in which boric acid exists in solution and the one in which it escapes from solution.

The first point can be settled by a determination of the boiling-point elevation or vapor-tension lowering of boric acid solutions. Measurements of this sort have shown that H_3BO_3 molecules exist in dilute solution. As the solution becomes more concentrated the vapor-tension lowering no longer corresponds to this formula; the decrease in the lowering indicates that the number of molecules of dissolved substance has grown less, i.e. some such change as $4H_3BO_3 = H_2B_4O_7 + 5H_2O$ has occurred.

If H_3BO_3 molecules volatilize with the water, the concentrations of boric acid in the solution and in the vapor must, according to HENRY's law, maintain a constant ratio, independent of the amount of boric acid present. This was found to be true for dilute solutions but not for concentrated ones, which is in agreement with the experiments on vapor-tension lowering, because there also the concentration of the acid in the vapor remained proportional to its concentration in the solution. It is therefore demonstrated that the compound which escapes with the steam is boric acid, H_3BO_3.

Boric acid crystallizes in lustrous laminæ, which feel greasy and are difficultly soluble in cold water (about 3% at ordinary temperatures). This solution acts as a weak antiseptic, for which purpose it is frequently used. At 100° boric acid loses 1 molecule H_2O, passing over into **metaboric acid**, HBO_2. At 140° **tetraboric acid**, $H_2B_4O_7$ ($= 4B(OH)_3 - 5H_2O$), is formed, the sodium salt of which is borax.

No salts of the normal boric acid, $B(OH)_3$, are known, but metaboric acid forms several. They are unstable and are converted by carbon dioxide into salts of tetraboric acid:

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

The best-known salt of boric acid is **borax**, $Na_2B_4O_7 \cdot 10H_2O$, often called *tinkal*. At present most of the borax on the market is made by boiling *colemanite*, $Ca_2B_6O_{11} \cdot 5H_2O$, found in California, or a similar borate, occurring in Chile, with soda. Borax swells greatly on heating; this is due to the escape of water of crystallization from the semi-molten salt. On continued heating it forms a vitreous mass. This glass has the property of dissolving metallic oxides, some of which give double borates of a characteristic color; hence its use in qualitative analysis. The same property makes it valuable in soldering; solder adheres only to the untarnished metal, so a little borax is placed on the surface of the metal and heated with the soldering-iron in order to remove the rust. The dissolving of metallic oxides is easily understood, when we write $Na_2B_4O_7$ as $2NaBO_2 + B_2O_3$; it is the boric oxide, B_2O_3, which can be regarded as combining with the metallic oxides to form salts.

Boric acid is a weak acid; its salts are therefore hydrolyzed quite perceptibly—more so, of course, as the dilution increases. This can be illustrated by a simple experiment devised many years ago by ROSE. To a concentrated solution of borax some litmus is added and then acetic acid until the litmus is just red; if the liquid is then diluted, it turns blue because the alkali is set free and boric acid has scarcely any effect on litmus.

Rather interesting, also, is the behavior of silver borate, which is deposited as a white salt on mixing concentrated solutions of borax and silver nitrate. When dilute solutions are mixed, however, a precipitate of grayish-brown silver oxide is formed, the silver borate being almost completely hydrolyzed in the dilute solution.

[On treating a mixture of boric acid and sodium peroxide with water a **perborate** is formed and crystals of the composition $NaBO_3 \cdot 4H_2O$ separate out. They are stable when solid but liberate oxygen from a warm solution. The solution contains hydrogen peroxide also.]

ALUMINIUM.

284. This metal does not occur native, but in combination it is found in large quantities and very widely diffused. *Corundum*, including the precious stones *sapphire* and *oriental ruby* and the natural abrasive *emery* (all noted for their hardness), consists of alumina Al_2O_3, colored by traces of other oxides. *Bauxite* is a hydrate of aluminium and iron. *Clay* and *kaolin* (China clay) are principally aluminium silicate. Many other minerals, such as *feldspar*, *mica*, etc., contain it as a base. A peculiar aluminium mineral, *cryolite* or *ice stone*, $3NaF \cdot AlF_3$, is found in Greenland.

The metal can be obtained from the chloride by reduction with sodium but at present it is produced exclusively by decomposing aluminium oxide with the electric current.

The most important commercial process is that of HALL (invented independently in Europe by HEROULT). Alumina is dissolved in a fused bath consisting of cryolite or an equivalent mixture. The process is carried out in a large carbon-lined pot, the inner surface of which constitutes the cathode. Carbon rods immersed in the bath serve as anodes. Fresh alumina is added from time to time and the metal is drawn off at the bottom periodically. The temperature is a little above the melting-point of cryolite. A current of several thousand amperes and less than 8 volts maintains the liquidity of the bath as well as effects the electrolysis.

The increased output due to improved methods has brought the price of the metal down from over $90 per pound in 1856 to about $0.20 at the present time, and the production is steadily increasing.

Aluminium is a silvery-white metal of low specific gravity (2.583). It is very ductile and malleable and fuses at about 700°.

It is permanent in the air, since it soon becomes coated with a firm thin layer of oxide. Small fragments burn with a bright light when heated in an oxygen atmosphere. It is not attacked by dilute nitric acid at ordinary temperatures and only slightly so by dilute sulphuric acid. Hydrochloric acid dissolves it readily, as does also caustic potash, hydrogen being evolved and aluminates formed in the latter case.

Before the efforts of **Deville** to bring about its preparation on a large scale were rewarded (1850) and before its properties were well known, great expectations were centred in this "silver out of clay." It was thought that if it could be cheaply prepared, it would displace the other metals and even compete with iron. Although the metal can now be produced at a really low price, those expectations are far from being fulfilled. This is undoubtedly due in large measure to the properties of the metal; its softness, inability to stand heavy strains or to resist the action of alkalies (soap) and acetic acid, greatly depreciates its supposed value. The cause of these disappointing facts lies partly, however, in slight impurities which are present in the commercial grades and seriously affect the properties of the metal. To these we may attribute the great difference of opinion in regard to its utility. A trace of nitrogen or carbon, for instance, greatly impairs its tensile strength; if traces of sodium are present, it is so readily attacked by water that the latter eats holes in sheets of the metal, although the pure metal is unaffected by water. However, aluminium bids fair to find extensive use in electrical work and lithography and for various purposes where lightness is important.

Various *alloys of aluminium* have also found a place in the arts. Among them mention may be made of aluminium bronze, which consists of copper and 5-12% aluminium. It can be easily cast and has a golden color and lustre. Its great firmness and elasticity render it valuable for physical instruments (balance beams) and watch springs. New alloys of aluminium are being constantly brought on the market: there is one with magnesium called *magnalium* and another with tungsten, for example.

Aluminium reduces many oxides (**Goldschmidt**) with a vigorous evolution of heat (§ 293). The reduction proceeds of itself after it has been started at a certain place in the mixture. For this purpose a primer is used consisting of a mixture of oxygen-producing substances, such as $KClO_3$, etc., and a piece of magnesium ribbon, which is ignited with a match. The heat that is thus evolved is used to heat iron bolts to white-heat and also for welding railroad rails, etc. The welding is accomplished by packing the rails in a mixture of iron oxide, sand, and aluminium powder together with a special sort of cement for making it compact. When this mass is ignited it continues to burn and heats the rails to glowing.

An *amalgam of aluminium* is easily prepared by introducing aluminium filings into a $\frac{1}{2}\%$ solution of corrosive sublimate. This amalgam decomposes water energetically at ordinary temperatures, liberating hydrogen and forming aluminium hydroxide. As neither basic nor acid substances go into solution, it is a *neutral reducing-agent.* The cause of this energetic reaction is due to the circumstance that the mercury hinders the formation of a thin firm coating of oxide over the surface of the metal, which would otherwise protect it from further oxidation.

Compounds of Aluminium.

285. The only known *oxide* of aluminium is **alumina,** Al_2O_3, which is formed on heating aluminium salts or the hydroxide. It is a white amorphous powder, readily soluble in acids; however, after it has been strongly ignited it is no longer soluble and must then be disintegrated by fusion with potassium hydroxide or acid potassium sulphate. It is found crystallized in nature (§ 284).

Aluminium hydroxide, $Al_2O_3 \cdot nH_2O$, is deposited as a hydrogel (§ 195) when a solution of an aluminium salt is treated with ammonia. In the decomposition of the aluminates it is obtained as a white powder. A hydrate with a low percentage of water, $Al_2O_3 \cdot 2H_2O$, *bauxite,* occurs in France and different parts of the United States in large deposits. Aluminium hydroxide is both weakly acidic and weakly basic in character. Its salts with acids suffer partial hydrolysis in aqueous solution and hence react acid (§ 239). It dissolves in alkalies to form *aluminates,* such as AlO_2K, AlO_2Na, and AlO_3Na_3, which are deposited in the amorphous state when alcohol is added to their aqueous solutions. They are decomposed by atmospheric carbonic acid.

Aluminium hydroxide is insoluble in water but dissolves in a solution of aluminium chloride. By subjecting this solution to dialysis, it is possible to get rid of the hydrochloric acid (which is present because of hydrolytic dissociation) entirely and thus obtain a colloidal solution of the hydroxide. Aluminium hydroxide does not form salts with weak acids.

Aluminium chloride, $AlCl_3$, is most conveniently prepared by passing dry hydrochloric acid gas over aluminium filings in a tube of porcelain or glass and collecting the sublimed product in a wide-mouthed bottle (see Fig. 74). After the tube has been heated to a sufficiently high temperature to start the reaction, no further heating is required; however, it is more practicable to continue heating in order to collect the chloride in the receiver.

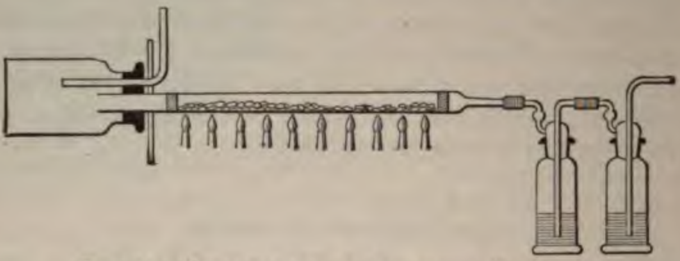


FIG. 74.—PREPARATION OF ALUMINIUM CHLORIDE.

Aluminium chloride is very hygroscopic. The aqueous solution hydrolyzes so readily, depositing alumina, that it can only be preserved by the addition of an excess of hydrochloric acid. Such a solution does not yield aluminium chloride on evaporation, since it decomposes completely into the hydroxide and hydrochloric acid on account of the continued removal of the latter dissociation product. The vapor density of the chloride up to 400° corresponds to the formula Al_2Cl_6, above 760° to $AlCl_3$. With the chlorides of potassium and sodium, aluminium chloride forms compounds such as $AlCl_3 \cdot KCl$, whose solutions can be evaporated without decomposition. Compounds such as $AlCl_3 \cdot PCl_3$, $AlCl_3 \cdot POCl_3$, etc., have also been prepared. In organic chemistry anhydrous aluminium chloride is of great value in synthetical work.

Aluminium sulphate, $Al_2(SO_4)_3 \cdot 16H_2O$, is obtained by treating clay with concentrated sulphuric acid; the product is dissolved in water and allowed to crystallize. Aluminium sulphate unites with the alkali salts to form double salts of the general type:

$$\overset{\mathrm{I}}{R}_2SO_4 \cdot \overset{\mathrm{III}}{R}'_2(SO_4)_3 \cdot 24H_2O,$$

which are known as **alums.** R may be either K, Na, NH_4, Cs, Rb, Tl, or an organic base; R′ may be Fe (ic) or Cr, instead of Al. The alums all crystallize in octahedrons and cubes, which often grow to large dimensions; they form mixed crystals readily. Ordinary alum (potassium alum) is used as a mordant in dyeing (ORG. CHEM., § 357), but it is being gradually superseded as such by aluminium sulphate and sodium aluminate. In the vicinity of Rome the mineral *alunite,* or *alum stone,* is found, whose composition is $K(AlO_2H_2)_3(SO_4)_2$; from it a much sought variety of alum is made. Alum is also made from cryolite, etc.

When two salts combine we may have one of two results: either the new salt which is formed gives ions in dilute aqueous solution that differ from those of the two salts, or it gives the same ions. A good example of the former case is yellow prussiate of potash; it gives neither ferrous ions nor cyanide ions, so that it must be regarded as $K_4[Fe(CN)_6]$. Such salts are termed complex. The second case is illustrated by the alums. A dilute alum solution exhibits all the reactions which characterize its components and its conductivity is the mean of the two separate salts for the same concentration. When the union is of this sort we have what is called a double salt. Between the two kinds there are salts of an intermediate nature which form not only complex ions but also the original ions to a greater or less extent. The copper-ammonia compounds (§ 244) behave in this way.

286. **Aluminium silicate,** *kaolin,* is formed in nature by the weathering of the numerous alkali-alumina double silicates, the alkali silicate being dissolved out, leaving the insoluble aluminium silicate. Clay is aluminium silicate; it is usually colored brown by iron oxide. It is the essential raw material of the ceramic industries, being used both for rough bricks and the finest china-ware; of course the better grades require better sorts of clay. Bricks are molded out of ferruginous and calcareous clays (loam) and then baked ("burned," or "fired") till they become firm. Under the head of *earthenware,* or porous ware (faïence, majolica, etc., and common crockery) we include all articles which consist of burned clay (frequently mixed with quartz), are porous and display an earthy fracture and which are covered with a glaze of easily fusible silicates. The glaze is produced by introducing salt into the kiln. The hot steam causes the formation of hydrochloric acid and sodium hydroxide, which unite with the clay to form sodium aluminium silicate. In *porcelain* the pores of the earthen mass are completely filled with fused silicate, as a result of the addition

of feldspar and quartz before the burning. The less of such admixtures is present the more difficult the porcelain is to burn and the less sensitive it is to changes of temperature.

Clay is the most widely diffused refractory material; it resists not only high temperatures and sudden changes of temperature, but chemical action as well.

Ultramarine is a very beautiful blue pigment, which is prepared artificially by heating a mixture of clay, soda, sulphur and wood charcoal in the absence of air. It occurs in nature as *lapis lazuli*. It is usually regarded as a compound of sodium aluminium silicate with polysulphides of sodium. This is indicated by the fact that it is attacked by acids with the evolution of hydrogen sulphide and the disappearance of the color, while it is unaffected by alkalies. It is still uncertain what substance gives the pigment its blue color.

GALLIUM, INDIUM, THALLIUM.

287. The existence of **gallium** was predicted by MENDELÉEFF (§ 217) in the same manner as that of germanium. The hypothetical *eka-aluminium* was discovered in 1875 by LECOQ DE BOISBAUDRAN in a zinc blende by means of spectrum analysis. Its spectrum consists of two violet lines. It is a very rare element. The metal is white, melts as low as 30° and has a specific gravity of 5.9. It is only superficially oxidized by the air and is not attacked by water. Like aluminium, it is only slightly affected by nitric acid but dissolves readily in hydrochloric acid as well as ammonia and potassium hydroxide. It forms alloys with aluminium, which, when the proportion of aluminium is small, are liquid at ordinary temperatures because of the depression of the melting-point of gallium, and it decomposes water almost as readily as sodium.

In its compounds, also, gallium displays much analogy with aluminium. The **hydroxide** dissolves in alkalies. The **chloride**, $GaCl_3$, fumes in the air like $AlCl_3$ and its aqueous solution yields hydrochloric acid on evaporation. The **sulphate** gives an **alum**, $Ga_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, with ammonium sulphate. Hydrogen sulphide precipitates gallium only from an acetic acid solution, in which respect gallium resembles zinc (§ 269).

Indium has already been referred to in the discussion of the periodic system (§ 216), so that it will be passed over here with a brief description. It was discovered through its spectrum, a blue line. This element, too, occurs very rarely, being found in certain *blendes*. The metal is white; m.-pt., 176°; sp. g., 7.42. It is permanent in the air; heated to a high temperature it burns with a blue flame to the **oxide** In_2O_3. The **chloride** $InCl_3$ is hygroscopic; its aqueous solution does not decompose on evaporation. The **sulphate** forms an alum with ammonium sulphate. The **hydroxide** dissolves in alkalies.

288. Thallium is the most common of these three elements, notwithstanding it always occurs in limited amounts. It is occasionally found in the "*Abraum salts*" *carnallite* and *sylvite* and frequently also in different native sulphides. When the zinc blendes are roasted in sulphuric acid factories the thallium goes off with the fumes and settles in the flue dust and chamber mud. From these deposits it is obtained by boiling with dilute sulphuric acid and precipitating with hydrochloric (or better hydriodic) acid, whereupon the sparingly soluble chloride (or iodide) is deposited. This element was also discovered with the spectroscope (CROOKES); its spectrum is a bright green line.

Thallium is a soft metal, about like sodium, and has a bluish color like lead. Sp. g., 11.8; m.-pt., 290°. In moist air it oxidizes very rapidly at the surface; but it does not decompose water at ordinary temperatures. When heated it burns with a beautiful green flame. Sulphuric and nitric acids dissolve it readily, but hydrochloric acid acts very slowly because of the slight solubility of the chloride.

There are two sets of compounds: the *thallous* compounds, derived from the oxide Tl_2O, and the *thallic* compounds, from the oxide Tl_2O_3. The former resemble those of the alkalies and silver very much. This similarity shows itself, for instance, in the solubility of the hydroxide and the carbonate, whose solutions react alkaline. Moreover, many thallium salts are isomorphous with potassium salts and, like the latter, give double salts with platinum chloride, e.g. Tl_2PtCl_6. Further there is an alum $Tl_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, as well as other double sulphates, e.g. $Tl_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, which are analogous to the corresponding potassium double salts. On the other hand thallium resembles silver and lead in the small solubility of its halides (the iodide is the least, and the chloride the most, soluble) and also in respect to the order of solubility of these compounds.

In the thallic compounds the element is trivalent, like the other elements of the group; furthermore, like the compounds of the latter, the thallic compounds readily form complex salts, and undergo considerable hydrolysis when dissolved in water.

SUMMARY OF THE GROUP.

289. The five elements last considered, B, Al, Ga, In, Tl, form a natural group, in which the last three display particular similarity to each other in their physical properties. Something analogous was observed with copper, silver and gold in the first group and with zinc, cadmium and mercury in the second group. The following table affords a brief comparison of certain physical data:

	B	Al	Ga	In	Tl
Atomic weight......	11.0	27.1	70	115	204.1
Specific gravity.....	2.45	2.58	5.9	7.4	11.8
Melting-point.......	very high	700°	30°	176°	290°

In the spectra of Ga, In and Tl it is again noticeable that the lines move towards the red end as the atomic weight increases (§ 265).

As to their chemical nature it may be remarked that all the elements of this group are trivalent and that the basicity of their oxides increases with rising atomic weight; boron hydroxide (boric acid) has exclusively acid properties, but the hydroxides of the other elements, even $Tl(OH)_3$, are also soluble in alkalies. As most of the lower oxides of the metals are more strongly basic than the higher oxides, it is not strange that thallous hydroxide is a strong base.

THE RARE EARTHS.

290. In the middle of the periodic table (p. 301) are located a number of elements, which are classed under the term "rare earths." There is still much uncertainty in regard to some of them, particularly as to their elemental nature. This is due in large measure to the great similarity between the elements and the consequent difficulty in separating them. They may be arranged in two groups: the cerium group containing the elements lanthanum, cerium, praseodymium, neodymium and samarium; and the yttrium group containing europium, terbium, dysprosium, holmium, yttrium, gadolinium, erbium, thulium and ytterbium.

These elements occur in various rare minerals which have been found principally in Sweden and Greenland, viz., *cerite, gadolinite, euxenite, orthite*, etc.

Since the use of the oxides of cerium and thorium in the incandescent gas-light of Auer von Welsbach has created a demand for them, minerals in which the rare earths occur are being ardently sought. The interesting fact has developed that they are by no means so "rare" as was supposed. An especially rich source of these earths has been found in *monazite sand*, which occurs in rather large quantities in the United States (production 900,000 lbs. annually), Canada and Brazil. It consists chiefly of a phosphate of Ca, La, Di, Y and Er, with varying amounts of thorium silicate and thorium phosphate.

In order to isolate the rare earths from these minerals the latter are powdered very finely and heated to faint-red heat with concentrated sulphuric acid. Thus the rare earths are changed into sulphates and the silicic acid is converted into the insoluble condition. The sulphates are then taken up in ice-water, in which they dissolve much more readily than in warm water (since a difficultly soluble hydrate is formed at a higher temperature). From this cold solution they can be precipitated with oxalic acid, their oxalates being almost insoluble even in dilute acids. Thus they are freed from Ca, Fe, etc. The oxalates are then converted into oxides by heating.

The separation of these oxides is a more difficult task. Various methods are in use, by which the separation of the ceric earths is fairly well accomplished; but for the numerous ytteric earths no successful method has yet been devised. Some of the methods employed for the ceric earths are as follows: The insolubility of the sulphates of cerium, lanthanum and didymium in a saturated sodium sulphate solution (by reason of the formation of double salts) is made use of to separate them from erbium, ytterbium and yttrium. The nitrates of the various metals of this group differ markedly in their stability on heating; hence another method of separation has been devised, by which the nitrates are decomposed one after another by heating and those that remain undecomposed after each successive heating are extracted with water. A third method is the fractional precipitation of the solutions with ammonia. Further, by fractional precipitation with potassium chromate (the insoluble neutral chromates being deposited), separations can be accomplished which are otherwise very difficult.

The ytteric earths are separated after Urbain by mixing the aqueous solution of their nitrates with bismuth nitrate, which is isomorphous with them. From this solution they separate out as mixed crystals with the bismuth nitrate, the different kinds of mixed crystals having different solubilities. If a fractional crystallization is conducted, certain of the rare earths accumulate in the first crystallizations, others in the last crystallizations, the middle ones consisting almost wholly of bismuth nitrate.

Most of the rare earth metals form only one oxide, having the formula M_2O_3; cerium, praseodymium and neodymium have higher oxides as well; of these CeO_2 is able to form salts.

The best method of detecting these metals is by spectroscopy. The spectra of the ceric metals are satisfactorily known; those of the ytteric metals are not so well known. Many of the latter are characterized by absorption bands, thus dysprosium, holmium and thulium. Others, like yttrium gadolinium and ytterbium, whose oxides and salts are colorless, do not give an absorption spectrum, but their spark spectrum is characteristic. The spectra of the ytteric earths display a great many lines. Furthermore, investigations of the ultraviolet spectra (photographic) have furnished important information.

In addition to these kinds of spectra the phosphorescence spectrum should be mentioned as an important means of investigation, especially to determine the purity of these earths. When the earths are placed in an evacuated tube and exposed to the action of cathode rays, the earths become luminous, a phenomenon that is known as cathodic phosphorescence. The spectrum of the phosphorescence has characteristic lines. It has been proved that the perfectly pure earths do not show the phospherescence, but that it is caused by extremely slight admixtures of other earths. The maximum influence is caused in most cases by an admixture of 1-0.1%. The disappearance of the phosphorescence is therefore a means of telling when the earth is pure. On the other hand however, the characteristic phosphorescence spectrum can be used to recognize some of the earths.

Cerium occurs principally in *cerite* (as high as 60%). Its salts are colorless when pure and give no absorption spectrum (§ 263).

The metal looks like iron and is quite permanent in the air. At an elevated temperature it takes fire. It forms two sets of salts, the *cerous salts*, which can be derived from the oxide Ce_2O_3 and are colorless, and the *ceric salts*, derivable from CeO_2, which are yellow or brown. Cerium is thus quadrivalent (as the existence of the fluoride $CeF_4 \cdot H_2O$ also indicates) and so belongs to the fourth group of the periodic system. When chlorine is passed into an alkaline solution of a cerous salt a yellow precipitate of CeO_2 is obtained.

Lanthanum is only trivalent. Its oxide La_2O_3 and its salts are colorless when pure.

Didymium was formerly regarded as an element but AUER VON WELSBACH succeeded in splitting it up into two components, called **praseodymium** and **neodymium**. This can be accomplished by making use of the difference in solubility of their potassium double sulphates in a concentrated solution of potassium sulphate. The praseodymium salts are green and give green solutions; the neodymium salts have an amethyst color and give pink solutions. The absorption spectra of the two elements differ considerably.

Scandium is likewise a trivalent element. Its existence was predicted by MENDELÉEFF, who called it *ekaboron*. Its trivalence places it in the aluminium group. The hydroxide $Sc(OH)_3$ is gelatinous, but insoluble in an excess of alkali.

Ytterbium. — The oxide Yb_2O_3 is the main constituent of *erbia* (obtained from *euxenite* and *gadolinite*), which also contains the oxides of scandium, yttrium, erbium, etc. Ytterbia (oxide) is obtained by fractional heating of the nitrate mixture (see above). The salts of ytterbium are colorless and give no absorption spectrum.

The salts of **samarium** are yellow and have a characteristic absorption spectrum.

TITANIUM, ZIRCONIUM AND THORIUM.

291. These uncommon elements are related to carbon and silicon in the same way as K, Rb and Cs are to Li and Na, and as Ca, Sr and Ba are to Be and Mg. Titanium and zirconium still give acid-forming oxides, while thorium forms only basic oxides.

Titanium displays very close analogy to silicon; it frequently occurs with the latter but always in a small amount. The element can be obtained by reduction of the oxide with aluminium. It is white, very hard and extremely refractory. Sp. g. 4.87. **Titanium dioxide**, TiO_2, occurs in three modifications: *rutile*, *anatase* and *brookite*. **Titanium chloride**, $TiCl_4$, is prepared by passing chlorine over the **carbide**, which is prepared in the electric furnace. $TiCl_4$ is liquid and fumes in the air because of decomposition by atmospheric water into HCl and $Ti(OH)_4$. **Titanic acid**, $Ti(OH)_4$, separates out as a white amorphous powder when the hydrochloric acid solution of a titanate is treated with ammonia. This action is due to the weak basic character of ammonia and the weak acid nature of titanic acid; as a result the ammonium titanate is completely hydrolyzed (§ 239). Like silicic and stannic acids, titanic acid readily forms poly-acids (§ 195). It dissolves in alkalies to form titanates, which are also obtained by fusing TiO_2 with alkalies. On the other hand titanic acid dissolves in concentrated sulphuric acid; it then remains in solution even when poured into water, because the excess of sulphuric acid hinders hydrolytic dissociation. Higher as well as lower oxides of titanium are known. The lemon-yellow oxide TiO_3 is formed on treating the sulphuric acid solution of $Ti(OH)_4$ with hydrogen peroxide (§ 38).

Zirconium occurs in nature chiefly as *zircon*, $ZrSiO_4$. It is not reduced from the the oxide by aluminium. MOISSAN obtained zirconium carbide, CZr, from zircon directly by heating it with sugar charcoal in an electric furnace (1000 amp. and 40 volts) for ten minutes. The silicon for the most part volatilizes If the carbide is treated with chlorine at dull-red heat, it is converted into the chloride. **Zirconium chloride** behaves with water in the same way as $TiCl_4$ and $SnCl_4$. The **hydroxide**, $Zr(OH)_4$, is precipitated by ammonia from acid solutions as a voluminous mass. It is insoluble in alkalies, but on being fused with the latter it forms salts such as Na_2ZrO_3 and Na_4ZrO_4, which are decomposable by water. The basic character of the hydroxide is apparent from the fact that it gives a sulphate, $Zr(SO_4)_2$, with sulphuric acid, which can be recrystallized out of water. *Zirconia*, ZrO_2, emits a very bright light when heated strongly and can therefore be used advantageously instead of lime in the DRUMMOND light (§ 13).

Thorium is at present obtained mainly from monazite sand; it is also found in the *thorite* of Arendal. The hydroxide $Th(OH)_4$ is insoluble in alkalies. The sulphate crystallizes with $9H_2O$.

Thoria and ceria are the essential constituents of the *incandescent gas-light* of A. VON WELSBACH. A finely woven cotton "mantle" is saturated with a solution of the nitrates of thorium and cerium, in which the two are contained in such a proportion that after ignition the ash contains 98-99% thoria and 2-1% ceria. When this ashen mantle is heated to incandescence by a Bunsen burner it gives out an intense light. This is apparently due to the fact that such an ash-mantle emits only a small proportion of red rays and rays of still greater wave-length, but mainly gives out rays of shorter wave-length; hence very little, if any, energy is lost by the emission of feebly luminous rays. However, it is found that a mantle consisting of thoria or ceria alone or of the two oxides in a proportion different from the above produces very little light. So far as the ceria is concerned this is due to its being present in such an excess that it cannot all be raised by the flame to full incandescence. An analogous phenomenon is seen in an ordinary flame, which when smoking (i.e. when too much carbon is present) gives less light than when not smoking. That it is not the thoria which emits the light is proved by the fact that a mantle consisting chiefly of ceria and containing only 1-2% of thoria produces very little light.

We must therefore suppose that in the mantle minute particles of ceria are spread out upon the very poor heat-conductor, thoria; thus, since their mass is small, they are able to reach the high temperature at which they emit the desired bright light; for the brightness of a flame increases with about the fifth power of the temperature.

In the *incandescent electric light* of Nernst the incandescent body ("glower") has the form of a wire rod, prepared from a mixture of rare earths (Zr, Th, Yt, Ce, etc.) and glazed. Both ends of the rod are connected with the wires conveying the current. At ordinary temperatures the rod is a non-conductor, but if it is warmed (by a burning match, e.g.) a current begins to pass through (if the potential is high enough) in gradually increasing amount; this heats the glower still higher so that in a short time it reaches bright incandescence. The interesting feature of this lamp is that a substance which is a non-conductor at ordinary temperatures becomes a conductor at a higher temperature. In its more recent form the Nernst lamp is supplied with an automatic electric "heater" close to the wire, so that no "lighting" is required. By reason of its efficiency this lamp bids fair to be of considerable commercial importance. According to Nernst, the "glower" conducts the electricity by an electrolytic process and not like a metal. One of the grounds for this belief is the fact that the conductivity of a metal decreases as the temperature rises, but that in the case of electrolytes it increases. Moreover, the continued use of a direct current results in the deposition of metal at the cathode end of the rod.

Nernst also found that below 1700° pure oxides do not conduct the current perceptibly, while mixtures do. The case is entirely analogous to that of aqueous solutions. Pure water is a non-conductor; so is pure hydrogen chloride; only when they are mixed does conductivity appear. Similarly, both thoria and magnesia are non-conductors by themselves, but, if they are mixed, we have conductivity.

Thorium is one of the radio-active elements. It gives off an emanation and the latter yields an induced radio-activity; both disappear by radiation. The characteristic periods during which their radiation intensity decreases to half its original value are: for the emanation 55 seconds, and for the induced radio-activity 11 hours. These periods differ considerably from those of radium and the products of its decomposition. Ramsay and Hahn succeeded in separating from thoric oxide a compound whose activity was found to be 150,000 times as great as that of thoric oxide itself, and which is probably formed from thorium. It is called **radio-thorium.**

VANADIUM, NIOBIUM (Columbium), TANTALUM.

292. These rare elements are allied to nitrogen and phosphorus in their properties and the formulæ of their compounds. As in all the other groups the metallic character becomes more prominent as the atomic weight increases. All three are prepared by passing an electric current through rods of the oxides in a vacuum.

Vanadium, which occurs in certain iron ores and in *vanadinite,* a lead vanadate, is characterized by an abundance of compound-types. There are, for example, four chlorides: VCl_2, VCl_3, VCl_4 and VCl_5. An oxychloride, $VOCl_3$, also is known, which is decomposed by water like $POCl_3$. The highest oxide, V_2O_5, a brown substance, is an acid anhydride; it forms salts which may be derived from the acids H_3VO_4 (ortho-acid) and HVO_3, metavanadic acid, and is thus analogous to P_2O_5.

An important salt is the *ammonium metavanadate,* NH_4VO_3; it is insoluble in ammonium chloride solution, which property is valuable in separating vanadium from its ores. The latter are fused with caustic soda and saltpetre, producing sodium vanadate, which is extracted with water. On saturating this solution with ammonium chloride, NH_4VO_3 separates out after a while as a sandy powder. Heating converts it into V_2O_5. This also serves as the characteristic test for vanadic acid.

Vanadium is finding various uses, both as the brown oxide and in alloys. It is of some importance for the manufacture of special steels. Moreover it is much less rare than was supposed, for traces of it occur in many granitic and other rocks.

Niobium (frequently called *columbium*) and **tantalum** form volatile chlorides, $NbCl_5$ and $TaCl_5$, which (like PCl_5) are decomposed by water. Particularly characteristic of these elements are their double fluorides, $2KF \cdot NbOF_3$ and $2KF \cdot TaF_5$. The latter is difficultly soluble, the former readily soluble, in water. Use is made of these compounds in separating the two elements. The oxides Nb_2O_5 and Ta_2O_5 in the presence of bases form salts of niobic acid, H_3NbO_4, and tantalic acid, H_3TaO_4. The element niobium is obtained in the free state by heating niobic acid with sugar charcoal in the electric furnace. It then contains about 3% of carbon. As it is not attacked by acids, it resembles boron or silicon more than it does the metals.

Tantalum metal is also very indifferent to chemical reagents, though it absorbs hydrogen greedily and also forms carbides. M.-pt., 2300°.

It is malleable and ductile, giving a wire of higher tensile strength than steel. Recently very fine filaments of metallic tantalum have been employed in incandescent electric lamps instead of the carbon filaments, the consumption of energy per candle power being considerably reduced.

CHROMIUM GROUP.

Chromium.

293. This element occurs principally in *chromite*, $FeO \cdot Cr_2O_3$ (§ 294), and less commonly in *crocoïte*, $PbCrO_4$. The former serves exclusively for the preparation of chromium compounds; for this purpose it is very finely powdered and fused with an alkali, thus forming chromates, which are extracted with water.

The element has been known for a long time, but it was not until 1894 that it was prepared pure on a large scale by MOISSAN. He reduced chromium oxide, Cr_2O_3, with charcoal in the electric furnace. An easier method is that of GOLDSCHMIDT (§ 284), by which chromium oxide is reduced with aluminium filings. If care is taken to have an excess of chromium oxide present, the metal is obtained entirely free from aluminium.

The metal thus obtained is lustrous and takes a polish. It does not melt in the oxyhydrogen flame but is completely liquefied in the electric furnace. It does not scratch glass (although the carbide C_2Cr_3 scratches quartz and topaz). At ordinary temperatures its behavior is that of a precious metal, i.e., it is not in the least affected by the air.

Chromium forms three sets of compounds, derived from CrO, *chromous oxide;* Cr_2O_3, *chromic oxide;* and CrO_3, *chromic anhydride.*

CHROMOUS COMPOUNDS.

These compounds have a very strong tendency to absorb oxygen and go over into chromic compounds; hence they can only be preserved away from the air. A solution of the **chromous chloride,** $CrCl_2$, is obtained by reducing chromic chloride, Cr_2Cl_6, with zinc and sulphuric acid. It has a beautiful blue color, which soon turns to green because of oxidation. If the solution of chromous chloride is poured into a saturated solution of sodium acetate, **chromous acetate** is precipitated as a red crystalline powder, which is much more permanent in the air than the other chromium salts and can therefore be used for their preparation. The **hydroxide** $Cr(OH)_2$ is yellow.

CHROMIC COMPOUNDS.

294. Chromic oxide, Cr_2O_3, is formed by heating chromic anhydride, CrO_3, or ammonium chromate (§ 105). It can be obtained crystallized by passing chromyl chloride, CrO_2Cl_2, through a red-hot tube. The amorphous compound is green; the crystals are black. After ignition it is insoluble in acids. When fused with silicates it colors the latter green, whence its use as a pigment for coloring glass and chinaware (*chrome green*).

GUIGNET's *green*, a beautiful pigment, is prepared by fusing potassium dichromate (1 part) with boric acid (3 parts). The potassium borate is dissolved out with water, leaving the coloring substance, $Cr_2O_3 \cdot 2H_2O$.

The *hydrogel of chromic oxide*, $Cr_2O_3 \cdot nH_2O$, is precipitated when a chromium salt is treated with ammonia. It is light blue but dissolves in caustic potash or soda to a green solution. On boiling this solution a lower hydrate of another color is deposited. The cause of this precipitation is readily understood, if it is assumed that the saturated solution of the lower hydrate contains less chromium ions than that of the higher hydrate. The alkaline solution is thus supersaturated in respect to the lower hydrate and the latter must be deposited. The solubility of chromic hydroxide in alkalies shows its slightly acidic character; it can also form salts with other metals, most of which salts are derived from $CrO \cdot OH$. An example of this type is the mineral *chromite*.

Chromium hydroxide is only a weak base; it does not form salts with weak acids such as carbonic acid, sulphurous acid, etc. (*cf.* § 239).

Chromium chloride, $CrCl_3$, is prepared by heating a mixture of chromic oxide and carbon in a current of chlorine; it then sublimes in brilliant violet crystal-laminæ. Chromic chloride thus obtained dissolves in cold water very slowly, but if traces of chromous chloride are present it dissolves readily. According to OSTWALD, this is to be regarded as a catalytic acceleration of the velocity of solution. The resulting solution is green; on evaporation green deliquescent crystals of the composition $Cr_2Cl_6 \cdot 12H_2O$ separate out. These crystals are also obtained from the solution of the hydrogel in hydrochloric acid. At 1200–1300° the vapor density corresponds to the formula $CrCl_3$.

Chromic sulphate, $Cr_2(SO_4)_3$, like other chromium salts (nitrate, chrome alum, etc.), has the peculiar property of dissolving in cold water to a violet solution, which turns green on warming. On cooling, this green color changes back to violet (rather slowly with the sulphate solution but rapidly with other salts). On slowly evaporating the violet solution at room temperature the salt crystallizes out, the sulphate, for instance, with fifteen molecules of water; the green solution, however, yields only an amorphous viscid mass.

In investigating these phenomena the sulphate solution has been usually employed, since its green modification can be kept the longest. Experiments have shown that the process depends on a splitting off of sulphuric acid (1 mol. H_2SO_4 from 2 mols. sulphate) and that green "chrom-sulphuric acids" are formed, i.e. substances with a complex chrom-sulphuric acid ion, since they do not give tests for either chromium or sulphuric acid. Thus only one-third of the sulphuric acid can be precipitated from a green solution of the sulphate directly with barium chloride, or in other words, only a third of the SO_4-ions of the original violet solution are still present. The transition from the violet solution to the green can therefore be formulated in this way:

$$\underset{\text{violet}}{2Cr_2(SO_4)_3} + H_2O = H_2\mathit{SO_4} + \underset{\substack{\text{complex ion}\\ \text{green}}}{[Cr_4O(SO_4)_4]}\mathit{SO_4}.$$

Only those SO_4-groups in italics are precipitated.

In a moderate state of dilution these chrom-sulphuric acids are as strongly ionized as sulphuric acid itself.

An analogous behavior is shown by chromic chloride, $CrCl_3$. A violet solution of it can be obtained by treating the violet solution of the sulphate with the theoretical amount of barium chloride. The chlorine can then be completely precipitated with silver nitrate at ordinary temperatures. If the solution is boiled for a time, however, and then cooled, silver nitrate will precipitate only two of the three chlorine atoms directly under the same conditions; the third must have gone with chromium to form a complex ion.

Chrome alum, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, is best prepared by passing sulphur dioxide into a solution of potassium dichromate containing free sulphuric acid:

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 \cdot Cr_2(SO_4)_3 + H_2O.$$

It can be obtained in finely developed octahedrons with edges several centimeters in length. It is used in dyeing and tanning.

CHROMATES.

295. There are numerous salts of the formula M_2CrO_4 which are derived from the oxide CrO_3, chromic anhydride, as in the similar case of sulphuric anhydride, SO_3; but while in the latter case the sulphuric acid itself, H_2SO_4, is also a stable compound, chromic acid, H_2CrO_4, has not as yet been isolated. When an acid is added to a chromate only the anhydride is obtained; the acid H_2CrO_4 breaks up forthwith into water and anhydride. The salts of chromic acid are isomorphous with the corresponding sulphates.

Chromic anhydride is obtained on adding sulphuric acid to a concentrated solution of potassium dichromate; it separates out in the form of long red rhombic needles, which, when freed from all sulphuric acid, do not deliquesce in the air. They are readily soluble in water. Heating to 250° breaks them up into chromic oxide and oxygen:

$$2CrO_3 = Cr_2O_3 + 3O.$$

Chromium trioxide is a very powerful oxidizing-agent; its solution cannot be filtered through paper because it destroys the paper by oxidation. When strong alcohol is dropped on chromic anhydride it takes fire, chromic oxide (Cr_2O_3) being formed at the same time. Hydrochloric acid is oxidized to chlorine and water, sulphurous acid to sulphuric acid. On passing dry ammonia over CrO_3 crystals, the gas takes fire and the oxide is reduced. When heated with sulphuric acid it yields oxygen and chromium sulphate. Hydrogen sulphide reduces the aqueous solution, sulphur being deposited. Chromic anhydride thus displays various characteristics of peroxides such as PbO_2, BaO_2, etc.

In addition to the normal salts of chromic acid, e.g. K_2CrO_4, there are also dichromates, trichromates, etc., which can be regarded as combinations of one molecule of the neutral salt with one or more CrO_3 molecules:

$$K_2CrO_4 + CrO_3 = \underset{\text{Dichromate}}{K_2Cr_2O_7}; \quad K_2CrO_4 + 2CrO_3 = \underset{\text{Trichromate}}{K_2Cr_3O_{10}}, \text{ etc.}$$

If $\frac{1}{2}$ molecule of sulphuric acid is added to 1 molecule of chromate, the yellow color of the chromate solution is changed to the red color of the dichromate; a CrO_4-ion gives up its electrical charge and an atom of oxygen to the hydrogen ions of the free acid, thus yielding water and forming, together with a second CrO_4 ion, the red ion Cr_2O_7:

$$4K^{\cdot} + 2CrO_4'' + 2H^{\cdot} + SO_4'' = 4K^{\cdot} + Cr_2O_7'' + H_2O + SO_4''.$$

Acid salts of chromic acid do not exist on account of this reducing effect of the hydrogen ions on the CrO_4-ions, for which reason also free chromic acid, H_2CrO_4, is incapable of independent existence.

Chromic acid is a weak acid, since its insoluble (in water) salts, e.g. those of barium, lead and silver, are readily dissolved by strong acids (§ 146).

Alkali chromates are invariably obtained by fusing a chromium compound with an alkali carbonate and an oxidizing-agent. The latter is unnecessary when the fused mass can be brought sufficiently in contact with the oxygen of the air by stirring. Chromite is worked up commercially into chromates in this way; it is calcined with soda and lime above 1000° in a reverberatory furnace:

$$2Cr_2O_3 \cdot FeO + 4Na_2CO_3 + 4CaO + 7O = 4Na_2CrO_4 + 4CaCO_3 + Fe_2O_3.$$

The resulting sodium chromate is lixiviated and sulphuric acid is added to its solution; on evaporation **sodium dichromate,** $Na_2Cr_2O_7$, crystallizes out, and this can be converted into **potassium dichromate,** a well-known salt, by double decomposition with potassium chloride.

The fusion is much more readily accomplished when caustic potash (KOH) is used instead of soda (Na_2CO_3), probably because fused potassium hydroxide absorbs oxygen from the air and forms the peroxide, thus becoming a much more active oxygen-carrier than soda. Under these circumstances the oxidation proceeds rapidly and completely as low as 500°.

Potassium dichromate finds frequent use as an oxidizing-agent in sulphuric acid solution, being itself reduced to chromic sulphate:

$$K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O.$$

An important commercial task is the regeneration of the chromic acid from such a chromium sulphate solution. The method followed in the factories at Höchst, Germany, is an electrical one. The solution is electrolyzed between lead electrodes in a vessel containing a diaphragm (porous partition). By the action of the current chromic acid is formed at the anode, while at the cathode hydrogen is evolved. Besides this, a change occurs in the concentration of the sulphuric acid on both sides of the diaphragm; it becomes higher in the anode portion, and lower in the cathode portion. The liquid oxidized at the anode can be used for oxidizing purposes without any further preparation. The chromic acid is again reduced to chromic oxide, Cr_2O_3, and the reduced liquid is then introduced into the cathode portion, while the liquid which previously occupied that space, is brought over to the anode side of the diaphragm. When the current is again turned on, the liquid at the cathode, which at the beginning of this second operation is richer in sulphuric acid than the liquid at the anode, yields its surplus to the cathode liquid. In this way an accumulation of sulphuric acid is avoided, and the same liquid can really be used continuously as an oxidizing-agent.

The chromates are yellow (except silver chromate, which is red) and the dichromates are red. **Lead chromate,** $PbCrO_4$, is insoluble in water and is used as a pigment (*chrome yellow*).

On heating potassium dichromate with potassium chloride and sulphuric acid a dark-red liquid distils over, which has the composition CrO_2Cl_2 and the boiling-point 117° and must be considered as the chloride of chromic acid; it is called **chromyl chloride,** or chromium oxychloride:

$$K_2Cr_2O_7+4KCl+3H_2SO_4=2CrO_2Cl_2+3K_2SO_4+3H_2O.$$

Water breaks it up into CrO_3 and HCl.

The semi-chloride of chromic acid, $CrO_2<^{Cl}_{OH}$, is known only in the form of salts. The potassium salt, for example, is obtained by heating potassium dichromate with concentrated hydrochloric acid:

$$K_2Cr_2O_7+2HCl=2CrO_2<^{Cl}_{OK}+H_2O.$$

It crystallizes in red prisms.

On treating a chromic acid solution with hydrogen peroxide in excess a beautiful blue coloration appears, which is absorbed by ether on shaking. It is due to a **perchromic acid,** whose ammonium salt $NH_4CrO_5\cdot H_2O_2$ can be isolated as a violet-black powder similar to powdered potassium permanganate. In concentrated aqueous solution decomposition soon occurs, the dichromate being formed and oxygen given off.

Molybdenum.

296. This comparatively rare element is found in nature in *molybdenite,* MoS_2, and *wulfenite,* $PbMoO_4$. The former alone is used in preparing molybdenum and its compounds. It is roasted and so converted into the trioxide, MoO_3.

The element itself is obtained from its oxides or chlorides by heating them red-hot in a current of hydrogen. The product is a steel-gray powder which fuses with great difficulty to a silvery metallic mass. Sp. g. = 8.6. Heating in the air converts it into the trioxide. It is not attacked by hydrochloric or dilute sulphuric acid, but is readily dissolved by nitric and concentrated sulphuric acid. Molybdenum also has recently found a metallurgical use in varying the properties of steel.

This element is noted for the great variety of its compounds; some of the more important ones may be mentioned here.

In addition to the oxides Mo_2O_3 (weakly basic) and MoO_2 (indifferent) there is **molybdenum trioxide,** MoO_3, which, like CrO_3, is an acid anhydride. It is a white powder which turns yellow on heating. It is very sparingly soluble in water. With alkalies it forms *molybdates.* It has a tendency to form *poly-molybdates* even stronger than the similar tendency of chromic anhydride;

ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (derivable from the acid $7H_2MoO_4 - 4H_2O$), commonly known as "ammonium molybdate," is a typical example. The addition of a strong acid to a molybdate solution precipitates white, glistening crystal-laminæ of **molybdic acid,** H_2MoO_4, which dissolve in an excess of acid. A solution thus prepared from ammonium molybdate and an excess of nitric acid serves as a test-reagent for phosphoric acid, with which it forms a yellow precipitate of about the composition $(NH_4)_3PO_4 \cdot 14MoO_3 + 4H_2O$ on warming (*cf.* §§ 146 and 162).

Of the chlorides the compounds $MoCl_3$, $MoCl_4$, and $MoCl_5$ are known. In the oxychlorides $MoOCl_4$ and MoO_2Cl_2 molybdenum can be regarded as sexivalent.

The chloride $MoCl_2$ does not exist according to MUTHMANN (neither does MoO), but a chloride Mo_3Cl_6 is known.

A very *characteristic test* for *molybdic acid* (the most common molybdenum compound) is the following: the substance is mixed with zinc and sulphuric acid; at first a blue coloration (a molybdate of molybdic oxide) appears but it soon turns green and then brown. This brown coloration is due to a salt of the oxide Mo_2O_3.

TUNGSTEN.

297. The minerals in which this element chiefly occurs are *scheelite,* $CaWO_4$, *wolframite,* or *wolfram,* (Fe,Mn)WO_4, and *hübnerite,* $MnWO_4$. The metal is obtained pure by the method of GOLDSCHMIDT (§ 284), i.e. by the reduction of pure tungstic acid with aluminium filings. The temperature thus produced is not high enough, however, to convert the metal into a regulus, or matte. STAVENHAGEN raised the temperature very considerably by adding liquid air to the reduction mixture before ignition; under these conditions the separate particles of tungsten unite to form a fused regulus. The metal so obtained is very pure; sp. g., 16.6. It is malleable and scratches glass. In combination with carbon it is very much harder. It is very permanent in the air. Sulphuric acid, hydrochloric acid, aqua regia, and hydrofluoric acid attack it very slowly, but it rapidly dissolves in a mixture of hydrofluoric and nitric acids. Fused caustic potash dissolves it slowly with the evolution of hydrogen. Tungsten is employed in the iron industry, since a small percentage of tungsten increases the hardness of steel in a marked degree (*tungsten,* or *wolfram, steel*).

Tungsten, like chromium and molybdenum, is also characterized by an abundance of compound-types. The chlorides WCl_2, WCl_4, WCl_5, and WCl_6 are known to exist. The lower ones are prepared from the hexachloride by heating in a current of hydrogen or carbon dioxide. The hexachloride itself is formed by direct synthesis; it is a violet-black crystalline substance; water converts it into the anhydride, WO_3.

Tungstic anhydride, WO_3, is obtained by precipitating the hot solution of a tungstate with nitric acid. It is insoluble in water and acids but soluble in alkalies. The addition of an acid to the cold solution of a tungstate precipitates **tungstic acid**, $WO(OH)_4[=W(OH)_6-H_2O]$. The latter forms polyacids, like chromic and molybdic acids. Like molybdic acid also it has the property of uniting with phosphoric and arsenic acids to form complex phospho-tungstates and arseni-tungstates.—The following is a very *characteristic test for tungstates:* If stannous chloride is added to a tungstate solution, a yellow precipitate (WO_3) is produced. On the addition of hydrochloric acid and warming, a beautiful blue solution (W_2O_5) is obtained.

URANIUM.

298. The principal uranium mineral is *uraninite*, which usually contains some iron. The metal is obtained by heating the chloride with sodium or by the electrolysis of the chloride or by the reduction of the oxide with carbon in the electric furnace. It is silvery-white and has a specific gravity of 18.7. It is much more volatile than iron in the electric furnace. When it is in the form of a fine powder it burns in a current of oxygen as low as 170°. In the same state it decomposes water slowly at room temperature. When nitrogen is passed over uranium the two elements combine readily at 1000° to form a yellow **nitride**. Another interesting compound is the **carbide** C_3U_2 (obtained from uranium oxide and charcoal in the electric furnace), inasmuch as the addition of water yields not only methane but liquid and solid hydrocarbons.

Uranium forms two sets of compounds; in the *ous* compounds it is quadrivalent (UX_4), in the *ic* compounds sexivalent (UX_6). The former pass readily into the latter. The oxide UO_2 has an exclusively basic character; it is obtained by igniting the other oxides in a current of hydrogen. It was at one time regarded as the metal itself.

Uranic oxide, UO_3, is a yellow powder, prepared by heating the nitrate. The corresponding hydroxide, $U(OH)_6$, is not known, but salts of the compound $U(OH)_6-2H_2O=UO_2(OH)_2$ with acids have been prepared. Since the UO_2 group acts here as a bivalent radical it is called *uranyl* and its salts uranyl salts, e.g. $UO_2(NO_3)_2$, **uranyl nitrate**, crystallizing with $6H_2O$ in beautiful greenish-yellow prisms. Uranium trioxide also has somewhat the character of an acid anhydride; if caustic potash and soda are added to uranyl salt solutions yellow *uranates*

($K_2U_2O_7$ and $Na_2U_2O_7$) are precipitated, which are soluble in acids. Uraninite can be regarded as the uranate of uranous oxide, $U_3O_8 = 2UO_3 \cdot UO_2$. Both oxides are converted into this U_3O_8 oxide by heating in the air. Uranium salts are used to impart to glass a beautiful greenish-yellow fluorescence.

The *detection of uranyl salts* is accomplished with the aid of the precipitate, soluble in excess, which they give with ammonium carbonate and by the reddish-brown precipitate with potassium ferrocyanide.

SUMMARY OF THE GROUP.

299. The elements *chromium, molybdenum, tungsten,* and *uranium,* in connection with sulphur, constitute a natural group in the periodic system. Particularly in the higher oxides there is considerable analogy with the behavior of this metalloid. Their acids, for example, all have the formula H_2RO_4. Moreover sulphur also has the ability to form polyacids (pyrosulphuric acid) although it is not so prominent as in the first-named four elements. Several of their salts are isomorphous. The strength of the acids decreases, as in other groups, with rising atomic weight. Another characteristic of all the elements of this group is the great abundance of formula types; it is also very noticeable in the case of sulphur, whose acids are remarkably numerous. The physical properties of these elements have not yet been fully determined, but a few of them are given in the following table:

	Cr	Mo	W	U
Atomic weight	52.1	96.6	184	239.5
Specific gravity	6.7	8.6	16.6	18.7
Color	white	white	white	white
Melting-point	very high for all			

MANGANESE.

300. This element is widely diffused in nature. Its most important minerals are *pyrolusite*, MnO_2, *hausmannite*, Mn_3O_4, and *rhodochrosite*, $MnCO_3$.

The metal is of minor importance. It is best prepared by the Goldschmidt method, i.e. by reducing pyrolusite with aluminium powder, when it is obtained as a regulus of brilliant lustre. Sp. g. = 7.2–8.0. It undergoes surface oxidation readily in moist air, which gives the regulus an iridescence, and when finely divided decomposes boiling water. It dissolves in acids to form manganous salts.

Manganese forms several series of compounds: the *manganous* compounds of the type MnX_2; the *manganic* compounds, MnX_3; *manganic acid*, H_2MnO_4, which can be derived from an anhydride MnO_3; *permanganic* acid, $HMnO_4$ derivable from the oxide Mn_2O_7. Most of the familiar salts of this element are derived from **manganous oxide,** MnO. This oxide, which is prepared by heating the carbonate in the absence of air, is an amorphous green powder, that oxidizes readily in the air to the higher oxide Mn_3O_4. **Manganous hydroxide,** $Mn(OH)_2$, is white when freshly precipitated from solutions by an alkali but soon turns brown in the air because of the formation of manganic hydroxide, $Mn_2(OH)_6$.

The solutions of **manganous** salts are pink (color of the $Mn^{\cdot\cdot}$-ion). The **chloride,** $MnCl_2$, crystallizes with four molecules of water. It can be obtained anhydrous by heating the double salt $MnCl_2 \cdot 2NH_4Cl + H_2O$, since the hydrochloric acid set free hinders the hydrolytic dissociation of the chloride. The **sulphate,** $MnSO_4$, crystallizes below 6° with $7H_2O$, above this temperature with $5H_2O$. It forms double salts, such as $K_2SO_4 \cdot MnSO_4 + 6H_2O$, similar to those of magnesium and iron; they are moreover isomorphous with the latter.

Manganous sulphide, MnS, has a pinkish-white color, which distinguishes it from all other sulphides.

If ammonium chloride is added to the solution of a manganese salt, no hydroxide is precipitated by ammonia; this is analogous to what is observed with magnesium (§ 254). The solution is, however, readily oxidized by the oxygen of the air and brown manganic hydroxide is deposited.

The **manganic** ion $Mn^{\cdot\cdot\cdot}$ is only weakly basic. Its salts are almost completely hydrolyzed in aqueous solution. The sulphate gives alums with cæsium and rubidium sulphates, which are also very unstable.

Manganic oxide, Mn_2O_3, is obtained from any of the other oxides by heating in an oxygen current. Since dilute sulphuric acid reacts with it, giving manganous sulphate and manganese dioxide, the oxide Mn_2O_3 is often considered as $MnO \cdot MnO_2$. The corresponding **hydroxide** is soluble in cold hydrochloric acid to a dark-brown solution. It is not certain whether this solution contains Mn_2Cl_6 or $MnCl_2$ and $MnCl_4$; on being warmed it gives off chlorine and is then known to contain the manganous chloride.

Mangano-manganic oxide, Mn_3O_4 or $MnO \cdot Mn_2O_3$, is obtained on strongly igniting the other oxides in the air. It is a brownish-red powder. When heated with hydrochloric acid it yields chlorine.

Manganese di- (or **per-**) **oxide,** MnO_2, the best-known manganese mineral (*pyrolusite*), is commercially of great importance in the production of chlorine. In the cold it dissolves in hydrochloric acid to a very dark liquid, probably containing the tetrachloride, and gives off no chlorine; when warmed it decomposes into chlorine and manganous chloride (§ 25).

Since pyrolusite is comparatively expensive; various methods have been devised for reconverting the manganous chloride into the peroxide. One which is of practical importance is the WELDON process. An excess of milk of lime is added to the chloride solution, whereupon air is forced through the warmed liquid. The manganous hydroxide which is precipitated undergoes oxidation and is converted into calcium manganite, $CaMnO_3$ ($=CaO \cdot MnO_2$), which settles down as a black slimy mass:

$$MnCl_2 + 2CaO + O = CaMnO_3 + CaCl_2.$$

The calcium chloride solution is run off and the manganite is used for generating chlorine, since it acts towards hydrochloric acid like a mixture of lime and manganese dioxide.

The value of the peroxide depends on the amount of chlorine it can produce with hydrochloric acid. In order to determine this, the mineral, finely pulverized, is warmed with hydrochloric acid and the evolved chlorine passed into potassium iodide solution, whereupon an equivalent amount of iodine is liberated. This iodine can be titrated with thiosulphate (§ 93).

Manganic acid and Permanganic acid.

301. When manganese compounds are fused with potassium hydroxide in the air or, better, in the presence of an oxidizing-agent (potassium nitrate or chlorate) a green mass results, which is dissolved by cold water, forming a dark-green solution. On evaporating this solution in a vacuum dark-green rhombic prisms of **potas-**

sium manganate, K_2MnO_4, crystallize out, which have a metallic lustre and are isomorphous with potassium chromate. They dissolve in potassium or sodium hydroxide solutions without change, but are decomposed by water with the separation of manganese dioxide and the formation of **potassium permanganate,** $KMnO_4$, the latter giving the solution a deep violet color:

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + MnO_2 \cdot H_2O + 4KOH.$$

On account of these changes of color the manganate solution received the name *chamæleon minerale,* from the early chemists.

Both in the solution of a manganate and in that of a permanganate we have the anion MnO_4; in the former, however, it is bivalent, in the latter univalent. This causes the difference in the properties of the two ions; the univalent ion MnO_4' is deep red and resembles the perchloric acid ion in behavior, while the bivalent MnO_4'' is deep green and displays analogy to the SO_4'' ion of sulphuric acid. The bivalent ion MnO_4'' is only stable in alkaline liquids; it is converted by water (more easily by acids) into the univalent ion:

$$3K_2MnO_4 + 4HNO_3 = 2KMnO_4 + MnO_2 + 4KNO_3 + 2H_2O,$$

or, written in ions:

$$6K^{\cdot} + 3MnO_4'' + 4H^{\cdot} + 4NO_3' = 2K^{\cdot} + 2MnO_4' + MnO_2 + 4K^{\cdot} + 4NO_3' + 2H_2O.$$

The reaction obviously amounts to a formation of water by the four hydrogen ions and two oxygen atoms which they extract from a bivalent anion MnO_4'', the latter being reduced to MnO_2. Of the four negative charges which are required to neutralize the four positive charges of the hydrogen ions two are taken from this MnO_4 anion, which is reduced to MnO_2, and the remaining two from two other bivalent anions MnO_4'', which thus become univalent. The transformation of potassium manganate into the permanganate is effected commercially by passing ozone into its concentrated solution:

$$2K_2MnO_4 + O_3 = 2KMnO_4 + K_2O + O_2.$$

The permanganate crystallizes out of the solution and the resulting mother-liquor can at once be used with a fresh quantity of pyrolusite to prepare more manganate.

Potassium permanganate, $KMnO_4$, crystallizes in beautiful glistening greenish-black prisms of the rhombic system, which dissolve readily in water, forming a deep-violet liquid. This salt is isomorphous with potassium perchlorate. All solutions of permanganates display the same absorption spectrum, viz., five dark bands in the yellow and green, no matter what the base is. It is thus evident that the ion MnO_4' is really the coloring-agent.

The solution of potassium permanganate acts as a powerful oxidizing-agent; in acid solutions two $KMnO_4$ molecules yield five oxygen atoms:

$$2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O.$$

The process may be regarded as a transformation of the anhydride of permanganic acid, $Mn_2O_7(=2HMnO_4-H_2O)$, into two molecules of basic oxide, MnO, and five atoms of oxygen; thus: $Mn_2O_7=2MnO+5O$.

In neutral or alkaline solutions, however, two $KMnO_4$ molecules yield only three atoms of oxygen, manganese peroxide being deposited at the same time (transformation of Mn_2O_7 into $2MnO_2+3O$):

$$2KMnO_4+H_2O=2MnO_2+2KOH+3O.$$

Since in oxidations with potassium permanganate in acid solution the deep color of the permanganate is replaced by the very faint color of manganous sulphate, many substances can be titrated with potassium permanganate in acid solution without an indicator. Ferrous sulphate is oxidized to ferric sulphate; oxalic acid goes over into carbon dioxide and water; nitrous acid in very dilute solutions is converted into nitric acid (§ 126); from hydrogen peroxide water and oxygen gas are formed. All these reactions proceed quickly and quantitatively at ordinary temperatures so that they are suitable for titration.

Permanganic acid is known only in aqueous solution; however, its **anhydride**, Mn_2O_7, can be obtained. It is prepared by carefully treating dry permanganate with concentrated sulphuric acid. It is a volatile, brownish-green, oily liquid, whose vapor explodes easily, yielding oxygen and manganese dioxide.

Manganese occupies an isolated position in the periodic system. No elements are known which are related to it as the elements Mo, W and U are to chromium. Moreover, only in its highest stage of oxidation, permanganic acid, does it display analogy with the corresponding chlorine compound, $HClO_4$. The salts of both acids are isomorphous and both are powerful oxidizing-agents.

IRON.

302. Iron is the most useful metal, and is therefore prepared commercially on an enormous scale (approximately 50,000,000 metric tons a year). It occurs only rarely *native*, e.g. in meteoric rocks. In the form of oxides, sulphides and silicates it is widely diffused in nature and is found in very large quantities. The most important minerals for the iron industry are *magnetite*, Fe_3O_4, *hematite*, Fe_2O_3, and *siderite*, $FeCO_3$. The *pyrites* (FeS_2, etc.) are worked up into iron after they have been roasted in the sulphuric acid factories.

The **metallurgy of iron** is theoretically very simple; it is based on the ability of carbon to reduce the oxides of iron to the metal at an elevated temperature. This process (smelting) is carried out in *blast furnaces.*

The iron ore is first roasted (calcined) to remove volatile substances (H_2O, CO_2, S, As, etc.) and loosen up the mineral. Then it is crushed and mixed with a slag-forming substance (*flux*, see § 242), according to the grade of the ore. If the gangue, or earthy matrix, contains much silica or alumina, limestone or dolomite is employed as the fluxing-agent, but ores rich in lime or magnesia are mixed with quartz or aluminous ore to effect the necessary fusion and formation of slag (silicates of Al, Mg and Ca).

The blast furnace, previously warmed to the proper temperature or already in operation, is charged from above with alternate layers of coke and the mixture of ore and flux, both being introduced in "rounds," or "charges," of definite weight. (Sometimes charcoal or anthracite is used as fuel.) The modern furnaces (Fig. 75) are built of fire-brick encased in iron and are of much lighter construction than those formerly used. They vary greatly in size but consist mainly of a long shaft tapering towards both ends. In order to utilize the escaping hot gases (CO, etc.) an apparatus ("cup and cone") is fitted on the top to conduct them off and also allow the introduction of the charge. The air necessary for the process is forced in, hot, through pipes (*twyers*) at the bottom of the furnace. The burning coke produces carbon monoxide, which is the principal factor in the reduction of the ore:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

The reduced iron sinks downward and comes in contact with carbon at a high temperature; as a result some of the carbon is dissolved by it and its melting-point considerably depressed. When a definite stage is reached the fused iron is drawn off below. It is protected from atmospheric oxidation by the slag floating on it.

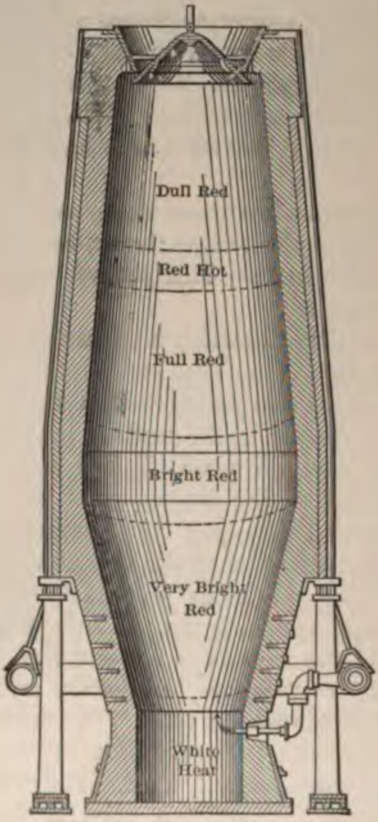


FIG. 75.—BLAST FURNACE.

The attempt to extract iron from its ores by electrical heating has met with success. STASSANO calculates on the basis of the analysis of the ore the additions which will be necessary to yield a slag as nearly as possible of the composition SiO_2+4 Base, compresses the finely powdered material to briquetts with the aid of tar in hydraulic presses, and smelts it in a specially constructed electric furnace.

303. It was stated above that the waste furnace-gases contain a considerable quantity of carbon monoxide; therefore a large amount of heat is lost, which could be utilized by burning the monoxide to dioxide. Supposing that this incomplete reaction was due to an incomplete contact of carbon monoxide and ferric oxide, manufacturers increased the dimensions of the blast furnaces, particularly in England and America, a height of thirty meters being not uncommon. The ratio of carbon monoxide to the dioxide in the escaping gases was not affected however; it was thus demonstrated by very expensive experience that the reduction of ferric oxide by carbon monoxide has a limit. A study of the laws of chemical equilibrium would have led to this conclusion much more quickly and above all much less expensively. These laws teach us that:

1. In the reduction of ferric oxide by carbon monoxide an equilibrium is established between this action and the oxidation of iron by carbon dioxide.

$$Fe_2O_3+3CO \rightleftarrows 2Fe+3CO_2.$$

2. The ratio $CO:CO_2$ must be independent of the pressure, since no change in the volume of the gas takes place (§ 51).

3. This ratio varies only slightly with the temperature, since very little heat is generated in the reaction.

An experimental investigation conducted at a few different temperatures and pressures would have sufficed to determine the ratio $CO:CO_2$. The result, when compared with the ratio $CO:CO_2$ of the waste gases, would thus have shown that little could be gained by an increase of the furnace dimensions. This illustrates in a very striking way the value of physical chemistry for industrial processes.

Efforts are now being made to utilize the waste gases in other ways, such as by burning them under the boilers of steam engines or in wind heaters (for heating the blast air, or "wind"). In recent years it has been found that greater efficiency is attained by using the hot waste-gases directly in gas engines for motive-power.

304. The properties of iron are influenced in great measure by the slight admixtures which it contains, particularly by the carbon. The percentage of carbon forms the ordinary basis of classification of the different grades of iron under the heads: pig iron and malleable iron; however, in the industrial world this classification is not always adhered to.

Pig iron, or **cast iron,** contains 2.3–5.1% carbon. It fuses very easily but there is no previous softening; hence it is not malleable. It is brittle. Pig iron is the direct product of the blast furnaces and the iron is therefore mixed with small amounts of silicon, phosphorus, sulphur, etc. The presence of manganese makes it coarsely crystalline and it is then known as *spiegel-eisen.* This is utilized mainly for steel.

Malleable iron, containing less than 2.3% carbon, is harder to fuse, but is extensible and malleable, and the more so the less the impurities. If the carbon amounts to 2.3–0.5%, the iron can be hardened; in this manner *steel* is obtained. If there is less than 0.5% carbon, it can no longer be hardened; this is *wrought iron.* It is obvious that between these main varieties there are numerous intermediate sorts, which are prepared in such a way as to suit the purpose for which they are intended.

The immense commercial importance of the iron-carbon system has led to extensive investigations regarding it, notwithstanding that such investigations are attended by great experimental difficulties, partly because of the very high temperatures involved. Because of these difficulties it is not yet possible to give an entirely satisfactory representation of the equilibrium conditions concerned. Bakhuis Roozeboom, however, has succeeded in reducing the observations of Roberts-Austen and others to the graphic representation which is shown in Fig. 76 and which indicates the behavior of the system in the main at least. To appreciate this diagram it is necessary in the first place to know a few general facts regarding the components that are now regarded as existing in the iron-carbon system. Distinction is made between: 1. *ferrite,* or chemically pure iron (pure wrought iron); 2. *martensite* (steel), a solid solution of carbon in iron. It is so regarded because microscopic studies have shown that martensite is always homogeneous in spite of its changing carbon content, which may be as high as 2%. 3. *cementite* (the commercial white cast iron), an iron-carbon compound of the formula Fe_3C; and 4. *perlite,* carboniferous iron (0.85%), that is seen under a high-power microscope to be heterogeneous and is regarded as a eutectic mixture of ferrite and cementite.

The solidification curve of a binary system (§ 237) does not take a normal course in the iron-carbon system. Two circumstances complicate the situation. The first is that pure iron does not separate out of the molten mass, but that we obtain the solid solution martensite. The second is that changes continue to occur in the cooling mass after complete solidification.

As for the first circumstance, the case is this: Let us assume that we have liquid iron with a carbon content below 4.3%. On cooling the liquid the iron begins to solidify at a definite temperature (the point c_1 in Fig. 76); however, it is not pure iron, but a solid solution of carbon in iron that separates out; its composition is shown in the diagram by the point d_1. If the carbon content of the fused iron is a different one, we have separating out at c_2, for example, the pure substance, whose composition is again given by the point d_2. Thus for every solidification point of the curve *AC* we can find a point d_1, d_2, etc., that gives the composition of the solid substance which begins to separate out. The curve *AD* is the geometrical locus of these points. If, therefore, a horizontal line is drawn through the triangle *ADC*, the point *c* gives the composition of the solid solution liquid which solidifies at the corresponding definite temperature (indicated by the ordinate) and the point *d* the composition of the solid solution which begins to separate out at that temperature. At *C* the eutectic point is reached. Along *CB* graphite separates out; at *C* itself a mixture of graphite and martensite, the composition being given by *D*. The point *C* is at 1130° and 4.3% of carbon. The martensite formed at this temperature contains 2% of carbon.

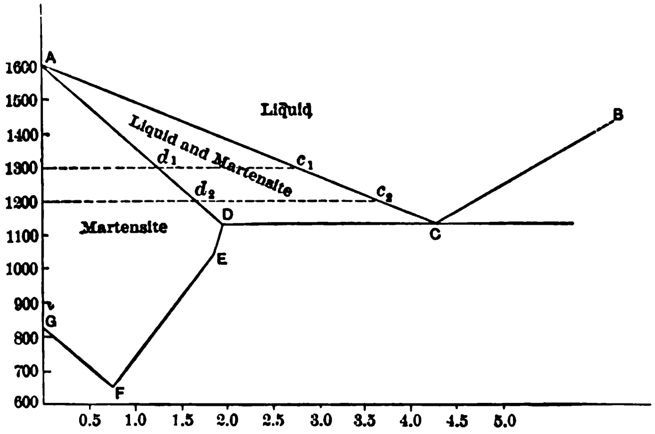


FIG. 76.—IRON-CARBON SYSTEM.

Below *DC* all is solid; but, as we have already explained, changes continue to occur in the solid mass. The curve *DE* gives the change in the composition of the solid solution with falling temperature. The course of this line to the left shows that carbon (graphite) separates out of the solid solution as far as *E*, when the temperature has reached 1000°, and the martensite contains only 1.8% of carbon. At 1000° a more fundamental transformation occurs, namely, the formation of cementite Fe_3C; the carbon passes from solid solution into chemical union with the iron. The curve *EF* represents the course of this transformation with falling temperature. Since cementite contains 6.6% of carbon and martensite at *E* only 1.8%, the formation of the first named substance must be associated with a considerable decrease of the carbon content of the solid solution, for which reason *EF* bears off rather rapidly to the left. At *F*, 690°, where the carbon content of martensite has gone down to 0.35% we have the last change that is known with certainty to occur in the solid mass. Here there is formed ferrite, together with cementite. If the carbon content is just 0.85%, martensite goes over at this temperature completely into a fine eutectic conglomerate of these two substances, which has been given the name "perlite." Finally, the curve *FG* indicates the compostion of the solid solutions from which ferrite separates out. Hence, if the martensite contains less than 0.85% of carbon, ferrite is deposited along *FG*, exactly as ice separates out of a dilute salt solution with falling temperature.

It is evident from the above that with slow cooling martensite entirely disappears. If the cooling is rapid, however, as in the hardening of steel, martensite can be brought to exist at ordinary temperatures even though it is in a metastable condition; its transformation velocity is then extremely small. If the hardened steel is reheated, it changes over partially into the soft conglomerate of ferrite and cementite; this is what takes place in the "tempering'' of steel.

Small admixtures of other elements have an effect on the properties of iron equally as great as that of carbon. The presence of *silicon* has about the same effect as that of carbon, but it is less intense. *Sulphur* even in a small amount renders the iron brittle when hot and, therefore, useless for forging. On this account sulphurous ores as such are unsuitable for the manufacture of iron. *Phosphorus* makes the iron brittle at ordinary temperatures. It should also be mentioned that as a general rule the effect of these admixtures is strongly modified by the presence of others.

305. From the crude pig iron, the direct product of the blast furnace, the other varieties of iron are prepared. For this purpose it must be freed from silicon, sulphur, phosphorus, etc., as well as from a large portion of its carbon. The most important process for accomplishing this commercially is the BESSEMER *process*. The pig iron is fused and run into a pear-shaped apparatus, or *converter* (Fig. 77), in the bottom of which are holes through which air is blown in. Thus by the oxidation of silicon, manganese and a little iron and without the use of fuel the temperature is raised high enough to effect the burning of the carbon. The BES-

SEMER process is easier controlled if the elimination of carbon is continued past the steel stage and until molten wrought iron is formed, whereupon enough carboniferous iron is added to furnish the desired percentage of carbon. At the completion of the process the converter is emptied by tipping.

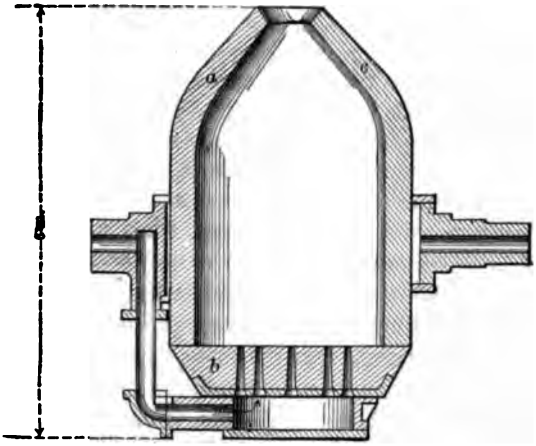


FIG. 77.—CONVERTER.

An objection to the BESSEMER process in its original form was that the phosphorus was not removed. The small amount of phosphorus present in iron might indeed be burned but the large amount of molten iron would at once reduce it back to phosphorus or to iron phosphide. This fault was corrected by an improvement devised by THOMAS and GILCHRIST. The interior lining (*a b c*, Fig. 77) consisted originally of nothing but refractory materials (ganister), rich in silica. This *acid* lining was replaced by them with a *basic* lining, consisting of clay and silica mixed with lime and magnesia and, in addition, lime was thrown into the converter with the pig iron. The phosphorus pentoxide produced by the combustion unites with the lime and magnesia and the phosphates are no longer reduced by the molten iron. As a by-product a slag (*Thomas slag*) is thus obtained, consisting of a basic phosphate, which, when ground very finely, is found to have great value as a fertilizer. It is brought on the market in enormous quantities.

The only successful rival of the **Bessemer** process is the **Siemens**, or *open-hearth, process.* By employing a special furnace and gaseous fuel a mixture of cast iron and wrought iron (together with some iron ore) in the proper proportions can be fused together so as to produce a very good steel. A basic lining can also be used with this process.

The production of wrought iron from pig iron is usually accomplished by the *puddling process.* Pig iron is melted in a reverberatory furnace lined with iron ore (oxide); the carbon and also the silicon are oxidized (and so removed) partly by the action of the air, but mainly by that of the ore, which is stirred in with the metal. The violent reaction due to escaping carbon monoxide gives the process the name of "pig-boiling." The iron is then allowed to become pasty, when it is worked up into large masses (*blooms*), which are removed and hammered and rolled. The cinder is thus squeezed out and the iron is formed into bars.

Efforts have been made to enhance certain properties of steel, which are valuable for particular purposes, by adding small amounts of other metals. A few of the results may be mentioned. The maximum hardness of steel is reached when it contains 1–2% carbon. If, however, some manganese (up to 8%) or chromium (up to 1%) is added, a much harder modification of steel is produced. The addition of nickel or aluminium makes wrought iron more malleable and elastic; as high as 3% nickel is sometimes added. The toughness of nickel steel makes it especially valuable for armor plate. Tungsten (*cf.* § 297) and molybdenum are also added for different purposes.

Further, the mode of manufacture can have great influence on the properties of iron. Steel, for instance, becomes very hard and brittle when it is suddenly cooled from a high temperature. If, however, it is then heated for a definite period and allowed to cool slowly, it becomes more or less *tempered* according to the temperature, i.e. it can be made to have any desired hardness and elasticity (within certain limits).

Chemically pure iron is obtained electrolytically and by reducing the oxide or chloride in a current of hydrogen. If the reduction takes place at a low temperature, the resulting iron powder is pyrophoric (§ 203). It is a silvery-white, lustrous metal with a specific gravity of 7.84 and a melting-point as high as 1600°. It is the most magnetic of the metals; pure iron and wrought iron can be magnetized only temporarily, steel, however, permanently. Iron is permanent in dry air or in water free from air (CO_2).

In moist air it rusts rapidly (§ 279), forming ferric hydroxide; as the rust does does not form a compact film, it keeps on forming.

The rusting of iron is greatly retarded by contact with water containing a little alkali or salts of alkaline reaction. In a soda solution, for instance, iron remains bright. The rusting of iron in contact with water can be explained by assuming that the oxygen dissolved in water endeavors to form hydroxyl ions with the hydrogen ions. In order to compensate their negative potential the iron sends its positive ions into the solution; in a short time the solubility product of ferric hydroxide is reached and the latter is deposited; in other words, the iron rusts. Now, if hydroxyl ions are previously introduced into the liquid by the addition of a base or a salt of alkaline reaction, the ionization of the water is diminished so much that the oxygen can find almost no hydrogen ions with which to form hydroxyl ions; therefore the iron does not send any more ions (§§ 276 and 277) into the solution and rusting is greatly retarded.

Iron dissolves readily in hydrochloric and sulphuric acids with the evolution of hydrogen. At red-heat it decomposes water, but the oxide is also reduced by hydrogen, so that an equilibrium results:

$$3Fe+4H_2O\rightleftarrows Fe_3O_4+4H_2.$$

In nitric acid (not too concentrated) iron dissolves readily with the evolution of nitric oxide, NO, but if the iron is first dipped in concentrated nitric acid and then rinsed off it becomes indifferent to the action of nitric acid. A thoroughly satisfactory explanation of this so-called "passivity" of iron has not yet been given.

Iron forms two sets of salts, the *ferrous* and the *ferric*.

Ferrous Compounds.

306. In the ferrous condition iron has only basic properties.

Ferrous oxide, FeO, is obtained by reducing ferric oxide with carbon monoxide. It is a black powder, which oxidizes easily on warming. **Ferrous hydroxide,** $Fe(OH)_2$, is precipitated from ferrous salt solutions as a pale green gelatinous substance by the addition of an alkali; it oxidizes very rapidly in the air to ferric hydroxide.

Ferrous chloride, $FeCl_2$, is formed on dissolving iron in hydrochloric acid; it crystallizes from this solution in green monoclinic prisms containing four molecules of water. The anhydrous salt is obtained as a white sublimate when iron is heated in dry hydrochloric acid gas. With potassium chloride and ammonium chloride ferrous chloride forms well crystallized double salts, e.g. $FeCl_2 \cdot 2KCl + 2H_2O$.

Ferrous sulphate, $FeSO_4 + 7H_2O$ (*green vitriol, copperas*), is the most familiar ferrous salt. It is prepared commercially, principally by dissolving up the waste metal of steel-wire factories in sulphuric acid, but also by partially roasting pyrite, whereby ferrous sulphide, FeS, is formed; the latter is left exposed to the air, when it oxidizes gradually to ferrous sulphate, which can be dissolved out. It crystallizes in large, bright green, monoclinic prisms, which effloresce slightly and at the same time become coated with a brown layer of basic ferric sulphate. The double salts such as $FeSO_4 \cdot (NH_4)_2SO_4 + 6H_2O$, MOHR's *salt*, are not so liable to oxidation; for this reason use is frequently made of MOHR's salt to standardize permanganate solutions (§ 301). Iron vitriol has numerous uses, e.g. for making ink, in dyeing, as a disinfectant (it absorbs both ammonia and sulphuretted hydrogen and is therefore used to dispel bad odors), etc., etc.

Ferrous carbonate is somewhat soluble in water containing carbonic acid and is therefore often present in natural waters (§ 17). The basic carbonate which is precipitated from a ferrous solution by soda oxidizes rapidly in the air to ferric hydroxide. The latter is also deposited from chalybeate waters on standing in the air for a time. Ferrous carbonate is only known as a mineral (*siderite*, § 302).

Ferric Compounds.

307. The ferric ion has only very slightly basic properties. Ferric salts of weak acids, such as carbonic acid, do not exist. In aqueous solution most of the ferric salts, even those of strong acids, are partially hydrolyzed. For that reason they are brownish-red, since this is the color of ferric hydroxide in colloidal solution. On the addition of an excess of sulphuric or nitric acid this color disappears, because there is no longer any hydrolysis. From this it appears that the ferric ion itself in aqueous solution is only slightly colored. The ferric salts are readily converted into ferrous salts by reducing-agents.

Ferric oxide, Fe_2O_3, iron sesquioxide, is formed on heating various iron compounds in the air and is manufactured by igniting green vitriol (§ 79). It is a dark-red powder and finds use as a pigment (*colcothar*) and in polishing glass, etc.

Ferric hydroxide separates out as a reddish-brown hydrogel, $Fe_2O_3+nH_2O$, when a ferric salt solution is treated with an alkali. The freshly precipitated hydrogel dissolves in a solution of ferric chloride or acetate. If this solution is dialyzed, a pure colloidal solution of the hydroxide is finally obtained; from this the hydrogel is reprecipitated by a small amount of alkali or acid.

Ferrous ferric oxide, Fe_3O_4, also called ferroso-ferric oxide or magnetic iron oxide, occurs in nature as *magnetite*. It is produced by heating iron in steam (§ 305).

Ferric chloride is obtained by passing chlorine into a solution of ferrous chloride. It crystallizes at different temperatures with different amounts of water, being an example of the case described on p. 339. On heating the salt hydrochloric acid escapes with the water of crystallization. Anhydrous ferric chloride can be prepared by heating iron in a current of dry chlorine.

Between 320° and 440° the vapor density is approximately that calculated for Fe_2Cl_6; between 750° and 1050° it falls to half, indicating a splitting off of chlorine or a dissociation into $2FeCl_3$.

The reddish-brown color of the aqueous solution of ferric chloride must be ascribed chiefly to un-ionized $FeCl_3$ molecules, for the salt has this same color when dissolved in ether, in which no ionization occurs. In part, also, this color comes from ferric hydroxide, which is formed by hydrolytic dissociation. This dissociation increases on warming the dilute aqueous solution, for a very dilute, almost colorless solution of ferric chloride turns reddish-brown on boiling. When cooled the liquid gradually resumes its original color.

Ferric sulphate, obtained by dissolving ferric oxide in sulphuric acid, forms alums, e.g. potassium iron alum, $K_2SO_4 \cdot Fe_2(SO_4)_3 + 24H_2O$.

When a ferrous salt is converted into a ferric salt in aqueous solution the bivalent ferrous ion is transformed into a trivalent ferric ion. The oxygen required for the conversion serves to oxidize the hydrogen ions of the acid (which must be added) to water, whereupon these hydrogen ions surrender their charge to the iron ions:

$$\underset{\text{Ferrous chloride}}{2(Fe^{\cdot\cdot}+2Cl')}+\underset{\text{Hydrochloric acid}}{2(H^{\cdot}+Cl')}+O=\underset{\text{Ferric chloride}}{2(Fe^{\cdot\cdot\cdot}+3Cl')}+H_2O.$$

Inversely, the reduction of ferric salts to ferrous salts can be explained by supposing that every ferric ion gives up a third of its charge to another atom and thus makes the latter an ion or neutralizes its charge.

Salts of iron are also known which are derived from the hypothetical oxide FeO_3. They are obtained by heating iron filings with saltpetre or passing chlorine into an alkaline suspension of the ferric oxide hydrogel. From such solutions **potassium ferrate**, K_2FeO_4, crystallizes out in dark-red prisms, isomorphous with the chromate and sulphate of potassium. These crystals are readily soluble in water, but their dark-red solution soon decomposes with the separation of ferric hydroxide and oxygen gas. The free ferric acid is unknown.

308. Iron unites with cyanogen to form complex and unusually stable anions, viz., the *ferrocyanic* ion $[Fe(CN)_6]''''$ and the *ferricyanic* ion $[Fe(CN)_6]'''$. Their best-known salts are potassium ferrocyanide, $K_4Fe(CN)_6\cdot 3H_2O$, and potassium ferricyanide, $K_3Fe(CN)_6$, the yellow and red prussiates of potash, respectively. The ionization of the complex ions themselves is so slight that they give none of the ordinary reactions for iron.

For the commercial *manufacture of yellow prussiate of potash* two processes are used: In the first, animal refuse (e.g. blood) is charred, yielding a black, highly nitrogenous mass. This is ignited with potash and iron filings. After cooling, hot water is added and the mixture filtered; from this filtrate the yellow prussiate crystallizes out on standing. This salt is not formed until the ignited mass is treated with water, for yellow prussiate is decomposed by heat and cannot therefore be present in the ignited mass. The latter probably contains potassium cyanide, iron and iron sulphide (animal refuse always contains sulphur compounds). These substances can interact according to the equations:

$$6KCN+FeS=K_4Fe(CN)_6+K_2S;$$
$$2KCN+Fe+H_2O=Fe(CN)_2+2KOH+H_2;$$
$$Fe(CN)_2+4KCN=K_4Fe(CN)_6$$

The second process is employed in illuminating-gas factories, for the unpurified gas contains a little cyanogen and prussic acid. After being freed from tar and ammonia it is passed through a washer (scrubber) containing a solution of potash in which ferrous carbonate (ferrous sulphate + potassium carbonate) is suspended. The following reactions, among others, are known to go on here:

$$FeCO_3 + 2HCN \rightleftarrows Fe(CN)_2 + H_2O + CO_2;$$
$$K_2CO_3 + 2HCN \rightleftarrows 2KCN + H_2O + CO_2.$$

Notwithstanding that these reactions are reversible, the hydrocyanic acid can be quantitatively fixed in this way, because the ferrous cyanide and potassium cyanide interact to form potassium ferrocyanide, which is but very slightly affected by carbon dioxide.

Potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$, forms large sulphur-colored crystals. Its three molecules of water can be expelled by gently warming, whereupon the salt is left as a white powder. It is not poisonous. With dilute sulphuric acid it produces prussic acid on warming; with concentrated sulphuric acid it yields carbon monoxide.

The free **ferrocyanic acid,** $H_4Fe(CN)_6$, separates out as a white crystalline precipitate when concentrated hydrochloric acid is added to a strong solution of potassium ferrocyanide. The precipitate soon turns blue in the air on account of the formation of Prussian blue (and partial decomposition as well). Various salts of this acid have characteristic colors and are insoluble; hence potassium ferrocyanide finds use in analysis. It is an interesting fact that this compound of iron can serve as a distinguishing reagent for ferrous and ferric compounds. The ferrous salt of ferrocyanic acid is white, but in the presence of air it passes rapidly over into the blue ferric salt (*Prussian blue*—a valuable pigment). The copper salt (§ 40) is brownish-red, the zinc salt white, etc.

Sodium nitroprusside, $Na_2Fe(CN)_5(NO) \cdot 2H_2O$, is formed by the action of nitric acid on sodium ferrocyanide. It crystallizes in ruby-red prisms and is a delicate reagent for alkali sulphides, whose solutions it colors violet.

Potassium ferricyanide, $K_3Fe(CN)_6$, red prussiate of potash, is formed from the yellow prussiate by treating a solution of the latter with chlorine or bromine:

$$K_4Fe(CN)_6 + Cl = KCl + K_3Fe(CN)_6.$$

It appears in dark-red crystals, which are readily soluble in water. The aqueous solution is unstable. The salt is often employed as an oxidizing-agent in alkaline solution, being itself converted into the ferrocyanide:

$$2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + O.$$

Iron forms some very peculiar compounds with carbon monoxide: $Fe(CO)_4$ and $Fe(CO)_5$. They are produced when carbon monoxide is passed over finely divided iron at 80°, or at ordinary temperatures if the gas is under pressure. Iron vessels which have held compressed illuminating-gas for some time are more or less attacked by the carbon monoxide of the gas, for if gas which has been kept in such a vessel is allowed to escape through a hot glass tube an iron mirror is formed on the inside of the tube.

COBALT AND NICKEL.

Cobalt.

309. The two best-known minerals of this metal are *smaltite*, $CoAs_2$, and *cobaltite*, or *cobalt glance*, CoAsS. The metal is obtained by calcining these minerals and reducing the resulting cobalto-cobaltic oxide, Co_3O_4, with carbon (or hydrogen). It has a pink color and a high lustre. Sp. g. 8.9. It is magnetic but much less so than iron. It is indifferent to the air. Hydrochloric and sulphuric acids dissolve it very slowly, but it readily forms a nitrate with nitric acid.

Besides the oxide, Co_3O_4, just referred to there are two others, **cobaltous oxide,** CoO, and **cobaltic oxide,** Co_2O_3. The salts are all cobaltous, corresponding to the bivalent ion $Co^{\cdot\cdot}$.

COBALTOUS COMPOUNDS.

The solutions of the salts are red; hence this is the color of the cobalt ion. The non-ionized cobalt salts are blue, e.g. the anhydrous $CoCl_2$, the silicate, etc. This difference in color enables us to tell readily whether a cobalt salt in solution is ionized or not. Thus in concentrated solutions, for instance, all those circumstances which reduce the ionization cause a change of color from red to blue, e.g. when a concentrated cobalt chloride solution is warmed or treated with hydrochloric acid. That the ionization is diminished by warming was mentioned in connection with cupric chloride (§ 244).

Cobaltous chloride, $CoCl_2 \cdot 6H_2O$, forms red monoclinic crystals, which turn blue on heating because of dehydration. **Cobalt sulphate,** $CoSO_4 \cdot 7H_2O$, is obtained in dark-red monoclinic prisms and is isomorphous with $FeSO_4 \cdot 7H_2O$. It forms double salts with alkali sulphates, e.g. $K_2SO_4 \cdot CoSO_4 + 6H_2O$. **Cobalt nitrate,** $Co(NO_3)_2 \cdot 6H_2O$, appears in red hygroscopic prisms. **Cobalt silicate** is very deep blue; hence its use for coloring glass. Pulverized cobalt silicate serves as a pigment (*smalt*) in painting, etc. THÉNARD'S *blue* is a pigment, obtained by igniting cobalt salts with alumina.

COBALTIC COMPOUNDS.

310. **Cobaltic oxide,** Co_2O_3, is obtained by igniting cobalt nitrate. It is a black powder, which passes over into cobalto-cobaltic oxide, Co_3O_4, at red heat and at white heat yields cobaltous oxide. It has the character of a peroxide; for by the addition of sulphuric acid it is converted into a cobaltous salt with the evolution of oxygen and it yields chlorine with hydrochloric acid. However, in cold dilute hydrochloric acid it dissolves without generating scarcely any chlorine.

Like iron, cobalt also forms complex ions, of which those with cyanogen are very stable. There are cobalt salts corresponding in composition to the yellow and the red prussiates of potash; the salt $K_3Co(CN)_6$, **potassium cobalticyanide,** crystallizes in colorless rhombic prisms. A peculiar complex ion occurs in the **potassium cobaltic nitrite,** $6KNO_2 \cdot Co_2(NO_2)_6 + nH_2O$, or $K_3 \cdot Co(NO_2)_6 + nH_2O$. It is formed on treating a solution of a cobalt salt with potassium nitrite and acetic acid. It is a yellow crystalline precipitate, which is very slightly soluble when potassium ions are present in excess in the liquid.

Cobalt also forms numerous complex ions with ammonia (§ 317).

Nickel.

311. Nickel occurs in *niccolite*, NiAs, and *nickel glance*, or *gersdorffite*, NiAsS. Especially important is the nickel silicate, *garnierite*, $H_2(Ni,Mg)SiO_4 + aq(?)$, which was discovered by GARNIER in New Caledonia, where it occurs in enormous quantities.

From this ore the nickel is obtained by a blast-furnace process similar to that for iron. The discovery of garnierite marked the beginning of a new era in the nickel industry. Much nickel is refined electrolytically.

Nickel is almost as white as silver, is very tough and has a high metallic lustre. Sp. g. = 8.8–9.1. It is feebly magnetic. It dissolves sparingly in hydrochloric and sulphuric acids but freely in nitric acid. It is permanent in the air.

It is employed in *nickel-plating* metallic objects and as a constituent of several *alloys*. German silver contains about 50% copper, 25% nickel, and 25% zinc. The nickel coins of Germany and the United States consist of 75% copper and 25% nickel. The use of nickel to vary the properties of iron has already been mentioned (§ 305).

The oxides of nickel, NiO and Ni_2O_3, are very similar to those of cobalt. The **nickelous oxide,** NiO, is the only one which forms salts.

Nickel chloride, $NiCl_2 \cdot 6H_2O$, yields green monoclinic prisms. When heated it turns yellow on account of loss of water.

Nickel sulphate, $NiSO_4 \cdot 7H_2O$, crystallizing in green rhombic prisms, is isomorphous with the corresponding ferrous and other salts and also forms analogous double salts.

Nickelic oxide, Ni_2O_3, also behaves as a peroxide; when warmed with hydrochloric acid it yields chlorine gas and nickel chloride.

Nickel carbonyl, $Ni(CO)_4$, is formed when carbon monoxide is led over finely divided nickel at ordinary temperatures. A state of equilibrium results here, viz.:

$$Ni + 4CO \rightleftarrows Ni(CO)_4,$$

which is displaced to the left with rising temperature, since the decomposition of nickel carbonyl takes place with a considerable absorption of heat (§ 103). Even as low as 60° the decomposition is of an explosive nature. It follows from the above equation that an increase of pressure (§ 122) must greatly increase the proportion of nickel carbonyl formed. Experiments confirming this showed at the same time that both the formation and the decomposition of this compound are very sensitive to traces of foreign substances.

Nickel carbonyl is a colorless, highly refractive liquid, which boils at 43° and congeals (crystalline) at −25°. When heated in the air it burns with a very sooty flame. This compound is of aid in extracting nickel from low-grade ores.

Nickel also forms a complex ion with cyanogen. On dissolving nickel cyanide in an excess of potassium cyanide the compound $K_2Ni(CN)_4$ is produced; it is, however, unstable, being decomposed by hydrochloric acid with the deposition of nickel cyanide, $Ni(CN)_2$.

312. A peculiar property is exhibited by the **sulphides** of cobalt and nickel, CoS and NiS. Hydrogen sulphide does not precipitate these sulphides from acid solutions, but, once precipitated (by ammonium sulphide), they are apparently not redissolved by dilute acids. This is contrary to the general rule of § 146 (see also § 73), for the sulphide should either be precipitated by hydrogen sulphide from a feebly acid solution (e.g. CuS), which is the case when the solubility product is very small, or else, when the solubility product is larger, it should dissolve in dilute acids, as is the case with ferrous sulphide. As a matter of fact, however, no real anomaly exists here, for the rate of solubility of these sulphides is only very slow under the usual conditions of the reaction, viz., dilute acid and room temperature. It increases with the concentration of the acid, temperature of reaction and fineness of grain of the precipitate. Nickel sulphide is soluble in alkali sulphides immediately upon its formation, but when once deposited in the solid state it is insoluble, or nearly so. This is seen when a nickel solution is treated with tartaric acid and then with an excess of sodium hydroxide, no nickelous hydroxide being precipitated. If hydrogen sulphide is passed into this solution a very dark-colored liquid results, from which nickel sulphide is deposited only very slowly. The same is true of cobalt in very dilute solution; in concentrated solution, however, the cobalt sulphide soon passes over into the insoluble modification and separates out.

PLATINUM METALS.

313. Under this head are included the metals *ruthenium, rhodium, palladium, osmium iridium* and *platinum.* They occur only in metallic form and are associated together in mixtures or combinations. The principal deposits are in the Ural and Caucasus, but smaller quantities are also found in California, Australia and Sumatra. The most important of these metals is

platinum. The platinum ores usually contain admixtures of iron, gold, etc.

This group falls into two subdivisions: the light metals, ruthenium, rhodium and palladium, and the heavy metals, osmium, iridium and platinum. The two sub-groups differ considerably in atomic weight and specific gravity:

	Light.			Heavy.		
	Ru	Rh	Pd	Os	Ir	Pt
Atomic weight....	101.7	103.0	106.5	191	193.0	194.8
Specific gravity...	12.26	12.1	11.9	22.4	22.38	21.45

A complete separation of the platinum metals from each other is extremely difficult, in the first place because their properties are very similar, and in the second place because their behavior is considerably modified by their mutual presence—a fact which indicates the existence of compounds with each other. Thus, for instance, platinum dissolves readily in aqua regia while pure iridium is insoluble in it; nevertheless when an alloy of the two metals is treated with aqua regia, some of the iridium is carried into solution. Further, the presence of iron (which occurs in all platinum ores) is often very disturbing; for example, pure platinum solutions are not precipitated by soda or barium carbonate, but if iron is present more or less platinum comes down with the hydroxide of iron. In spite of these difficulties platinum, palladium, rhodium and iridium can now be purchased in a remarkably pure state.

For the commercial preparation of pure platinum the impure metal is fused with six times its weight of lead, whereupon this alloy is granulated. On treating it with nitric acid the lead is dissolved out as well as the copper, palladium and some of the rhodium. The residue still contains some lead and appears as a black powder. This is next treated with dilute aqua regia, which dissolves all except the iridium. From this solution lead is first precipitated by sulphuric acid; then the platinum with ammonium chloride. The ammonium chloroplatinate obtained in this way may still contain some rhodium. In order to eliminate the latter the chloroplatinate is mixed with potassium bisulphate and some ammonium bisulphate and slowly raised to the temperature of red heat. By this process the platinum salt is converted into platinum sponge, while rhodium goes over into the bisulphate, which is readily removed with boiling water.

Ruthenium.

314. This steel-gray metal is hard, very brittle and very difficult to fuse, a temperature of at least 1800° being necessary. Even when finely divided it is but very sparingly soluble in aqua regia, forming Ru_2Cl_6, but when alloyed with platinum, it dissolves readily. The compound $RuCl_4$ is known only in double salts. As a powder the metal oxidizes in the air to RuO and Ru_2O_3. Ruthenium also forms characteristic salts, in which it plays the part of an acid.

Potassium ruthenate, K_2RuO_4, results from fusing ruthenium with caustic potash and saltpetre. It crystallizes with $1H_2O$ in black prisms of a greenish lustre. With water it forms a dark orange-colored solution. Its conduct reminds one of potassium manganate, for under the influence of dilute acids it is converted into **potassium perruthenate**, $KRuO_4$, with the simultaneous precipitation of a black oxide, Rh_2O_5 (or RuO_2?). It crystallizes in black octahedrons of metallic lustre, which dissolve in water to a dark-green solution. A peculiar compound is the **tetroxide**, RuO_4, which volatilizes when chlorine is passed into the concentrated solution of potassium ruthenate. It can be solidified by cooling, when it forms a golden crystalline mass, fusible at 25.5°. There is no acid corresponding to this oxide. RuO_4 is used for the preparation of pure ruthenium.

Osmium.

This metal is very analogous to ruthenium; it melts as high as 2500°. The chlorides $OsCl_2$ and $OsCl_4$ and the oxides OsO, Os_2O_3 and OsO_2 are known. The great similarity to ruthenium is especially noticeable in the highest oxides. Thus fusion with caustic potash and saltpetre produces **potassium osmiate**, K_2OsO_4, which crystallizes from aqueous solution in dark-violet octahedrons containing two molecules of water. The characteristic osmium compound is the **tetroxide**, OsO_4, formed by igniting finely powdered osmium in the air or by the action of chlorine on the metal in the presence of water. The aqueous solution of OsO_4 reacts neutral, but is often (wrongly) called osmic acid. It is employed in microscopy since organic substances (i.e. reducing-agents) reduce it to black osmium. No salts derived from OsO_4 are known. This compound is used in preparing pure osmium.

The metal itself now finds application in the osmium incandescent light of AUER VON WELSBACH, where a fine osmium wire is heated electrically to incandescence in an evacuated globe.

Rhodium.

The metal in the fused state has the appearance of aluminium and is just as extensible (malleable and ductile) as silver. It is prepared pure in the arts by way of the chloro-purpureo rhodium chloride, $Rh(NH_3)_5Cl_3$ (*cf.* § 317). Neither acids nor aqua regia affect it. When heated in the air it is oxidized to the rhodious oxide, RhO. It is able to absorb a considerable amount of hydrogen. The rhodic oxide, Rh_2O_3, yields salts with acids. Of the chlorides only Rh_2Cl_6 is known; this is obtained by direct synthesis as a reddish-brown substance; it forms soluble double salts with the alkali chlorides.

Iridium.

This very refractory metal is obtained from *iridosmine* by heating in a current of oxygen, when the osmium volatilizes as tetroxide. In the form of a platinum alloy it is employed in the manufacture of "platinum" crucibles, dishes, distilling-vessels for the concentration of sulphuric acid (§ 86), etc. The prototype of the meter at Paris is made of an alloy of 90% platinum and 10% iridium. The admixture of iridium makes the platinum more indifferent to chemical agents. When pure, iridium is not attacked by aqua regia.

Iridium forms two chlorides, Ir_2Cl_6 and $IrCl_4$. Both of them give double salts with the alkali chlorides; e.g. $Ir_2Cl_6 \cdot 6KCl + 6H_2O$ and $IrCl_4 \cdot 2KCl$. The former dissolves in water readily, the latter with difficulty. The tetrachloride appears as a black substance forming with water an intensely red solution. For this reason a platinum chloride solution which contains iridium has a much deeper color than a pure solution.

Palladium.

315. The silvery-white metal fuses at 1500°, i.e. more easily than platinum. When finely divided it dissolves in boiling concentrated hydrochloric, sulphuric and nitric acids. On ignition in the air it is at first oxidized, thus losing its lustre, but at a higher temperature the metallic lustre reappears. The most peculiar characteristic of the metal is its ability to *absorb hydrogen* in large quantities (*occlusion*). Freshly ignited palladium foil absorbs 370 times its own volume of hydrogen at room temperature. By making palladium foil the cathode in a water electrolysis apparatus the metal can be made to take up even 960 times its own volume. This absorption does not alter its metallic appearance. The absorbed hydrogen can all be expelled by heating in a vacuum.

It was formerly supposed that in this absorption a compound Pd_2H was formed. Investigations (by Roozeboom and Hoitsema) from the standpoint of the phase rule (§ 71) have, however, rendered the existence of this (or any similar) compound doubtful. In case a compound were formed, there would be two substances (Pd and H) and three phases (Pd, the supposed compound, and H) and we should have a complete heterogeneous equilibrium. Various states of affairs would then be possible. The relation between the pressure and the amount of gas at constant temperature could be represented graphically for a simple case thus: If the gas at first merely dissolves in the metal, the pressure must rise steadily with the amount of gas absorbed until the compound is formed, *a*, Fig. 78. This gas pressure must then remain constant while the absorbed gas volume increases until the metallic phase has completely disappeared by conversion into the hydride. Supposing that this were the case at *b*, hydrogen could still dissolve in the hydride, but the pressure of gas ought to increase from that point; in other words, the pressure curve should show abrupt bends at *a* and *b*.

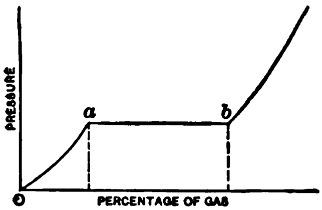


Fig. 78.

On the other hand, if no compound is formed and it is merely a matter of absorption, there are only two phases (gas and its solution) for the two substances, and therefore the equilibrium is incomplete; the pressure will steadily rise as the amount of gas increases and at no point will the curve suddenly change its direction.

The experiments showed that the pressure curves for various temperatures (between 0° and 190°) consist of three parts, viz., of two steep portions connected by a third middle portion, which runs almost horizontal at low temperatures. But at all investigated temperatures these portions were found to gradually pass into each other, so that the curve does not appear as in Fig. 78. These results point to the non-existence of any chemical compound; they indicate a continuous absorption, which is, however, distinguished from other known phenomena of this sort by the peculiar form of its pressure curve.

Palladium charged with hydrogen is a strong reducing-agent; chlorine and iodine are reduced by it (see § 200) to hydrogen chloride and hydrogen iodide, respectively, and ferric salts are reduced to ferrous salts.

Palladium forms two series of compounds, the *-ous*, PdX_2, and the *-ic*, PdX_4. A characteristic compound of the first series is **palladious**

Iodide, PdI_2, which is precipitated by potassium iodide from solutions of -ous salts as a black insoluble substance. This reaction is occasionally used to separate iodine from the other halogens, since their palladium compounds are readily soluble.—**Palladic chloride,** $PdCl_4$, is produced by dissolving the metal in aqua regia. With KCl or NH_4Cl it forms a difficultly soluble double chloride, K_2PdCl_6 or $(NH_4)_2PdCl_6$. On the evaporation of its solution $PdCl_4$ dissociates into $PdCl_2$ and Cl_2.

Platinum.

316. This metal, which is the principal constituent of the platinum ores, is obtained pure by the process explained in § 313. It fuses at about 1720° and is extremely malleable and ductile, hence it can be made into very fine wire and very thin foil. Since it becomes soft at red heat it can be easily worked. Alloyed with a few per cent. of iridium it finds various uses, especially for laboratory apparatus. When finely divided it absorbs oxygen (partially combining with it), a property to which is attributed the phenomenon that numerous oxidations proceed with unusual ease in the presence of platinum. Its use in gas-lighters depends on this property. When the metal is precipitated from its solutions by reducing-agents, it is frequently obtained as an extremely fine velvet-black powder, *platinum black*. When the double chloride $(NH_4)_2PtCl_6$ is ignited, the metal is left as a porous mass—*platinum sponge*. At red heat a platinum partition allows hydrogen to pass through, while other gases are held back. This is due to the formation of a compound or to the solubility of hydrogen in platinum. Various substances attack platinum at elevated temperatures, e.g. the hydroxides, cyanides and sulphides of the alkalies; hence these substances should not be fused in platinum vessels. This also applies to lead and other heavy metals, for they form low-melting alloys with platinum.

There are two sets of platinum compounds according to the general formula PtX_2 and PtX_4. The best-known platinum compound is **chlorplatinic acid,** H_2PtCl_6, obtained by dissolving platinum in aqua regia. When the solution is evaporated the chlorplatinic acid is left in the form of large, reddish-brown, very hygroscopic prisms. Its aqueous solution contains the anion $PtCl_6''$, for such an anion goes to the anode in an electrolysis; silver nitrate precipitates from the solution not silver chloride, which it would certainly do if free chlorine ions were present, but the compound

Ag_2PtCl_6. Two characteristic salts of this acid are those of potassium and ammonium; they are very difficultly soluble in water and insoluble in alcohol; when the aqueous solution is evaporated the salt remains in the form of small, but well-formed octahedrons of a golden hue. The potassium salt is often made use of in determining potassium when sodium is also present, the sodium platinic chloride being very soluble, even in alcohol.

Of the remaining platinum compounds a few may be referred to. If a solution of the above acid, H_2PtCl_6, is treated with sodium hydroxide and then with acetic acid, **platinum hydroxide,** $Pt(OH)_4$, is precipitated. It is soluble in strong acids and also in alkalies, so that basic as well as acidic properties must be ascribed to it (*platinic acid*). Salts of this acid are moreover formed when platinum is fused with alkalies. **Platinous chloride,** $PtCl_2$, is produced by heating chlorplatinic acid to 200° and in small amount, also, when the solution of this acid is strongly concentrated. It is a green powder, insoluble in water. With the alkali chlorides it gives soluble double salts, such as $PtCl_2 \cdot 2NaCl$. **Double cyanides** of platinum with many metals are also known, e.g. $K_2Pt(CN)_4 \cdot 3H_2O$, $BaPt(CN)_4 \cdot 4H_2O$, etc. The latter has come into prominence because of its ability to make Röntgen rays visible. All these double salts are noted for their beautiful colors and strong dichroism.

By forming an electric arc between platinum wires under distilled water BREDIG brought about such a minute division of the platinum that the particles would pass through a filter and no distinct particles could be detected in the liquid with the aid of the most powerful microscope. A platinum liquid of this sort has a deep-black color and a strong catalytic action, which resembles in many respects the action of organic ferments. This is noticeable in the extremely small quantity that is capable of exerting a catalytic influence; for instance, a liquid containing 1 gram-atom of platinum in 70 million liters of water accelerates the decomposition of hydrogen peroxide very perceptibly. The analogy is also supported by the fact that the catalytic effect of the platinum liquid, like that of organic ferments, alters slowly of itself but more rapidly on the addition of certain substances or on warming. Especially striking is the analogy as concerning the reduction of the catalytic effect by the addition of slight traces of certain "poisons": 10^{-6} gram-molecule HCN in a liter is sufficient to considerably diminish the effect and corrosive sublimate acts in much the same manner.

METAL-AMMONIA COMPOUNDS. WERNER'S EXTENSIONS OF THE NOTION OF VALENCE.

317. Several metals, notably those of the eighth group of the periodic system, are capable of forming complex compounds with ammonia and acid radicals. Such compounds have long been known, some having been prepared by the old master, Berzelius. The study of these substances occupied various investigators of the nineteenth century, especially Jörgensen. In recent years, however, this field has been explored and greatly extended by the investigations of Werner and his pupils, so that at the present time over 1700 compounds of the general type $MX_p(Am)_q$, are already known, M being a metal atom, X an acid radical and Am ammonia or an organic base (or even water). Chief credit is also due Werner for having taken up the theoretical study of the relationships between these compounds and, as a result, generalizations of considerable importance for the structure of inorganic compounds, especially the *complex salts*, have been established. The whole subject deserves a little attention at this point.

Concerning the methods of preparing these metal-ammonia compounds very little of a general nature can yet be stated. It is readily appreciated that the preparation of such a large number of complex compounds calls for the most diversified synthetical methods.

In order to acquire an insight into the nature of the compounds concerned we may first examine the trinitrito triammine cobalt, $Co(NH_3)_3(NO_2)_3$, which can be obtained by mixing cold solutions of cobalt chloride, ammonium chloride and sodium nitrite and treating the mixture with a current of air. The compound then separates out as a difficultly soluble crystalline powder. It can be recrystallized from hot water containing a little acetic acid, without liberating nitrous acid, and is not attacked by dilute mineral acids in the cold. The electrical conductance of its aqueous solution is approximately zero. Evidently, therefore, the substance lacks the ordinary properties of a nitrite; the NO_2-groups must be joined to the molecule differently than in the nitrites. The ammonia, too, is otherwise combined than in the ammonium salts. This follows at once from the fact that the compound is a non-electrolyte: furthermore, from the fact that the action of even concentrated acids is insufficient to split off ammonia. The NH_3-groups are not held by the acid radicals present in the molecule, for by energetic reactions it is possible to substitute other acid radicals for these without liberating the ammonia molecules. The supposition of an active participation of the acid radicals in the linkage of the NH_3-molecules is thus excluded. In deciding how the ammonias are connected to the molecule it is significant that the ammonia molecules can be replaced successively by other molecules. This shows that each ammonia molecule must be linked independently of the others in the complex molecule. About the only satisfactory explanation is that the NH_3-molecules are attached directly to the metal atom. Werner, however, makes the same assumption for the acid radicals in order to explain their abnormal behavior. This theory, whereby the special properties of the groups in compounds of the type $MX_p(NH_3)_q$ are explained on the assumption that these groups are in direct combination with the metal, has proved to be of great importance for the classification of these compounds. The acceptance of this principle, however, necessitates an *extension of the present notion of valence.* Cobalt, for example, is at most trivalent in its salts and oxides; but, if we assume a direct linkage to the metal of the three NH_3- and the three NO_2-groups, the cobalt must have a valence of six. These new-appearing affinities of the metal atom cannot offhand be classed with the ordinary valence bonds. For this reason it seems appropriate to assign a special name to them. In order to distinguish them from the ordinary valences, which are termed "principal" or "primary" valences, they are called "subordinate," or "secondary," valences.

Compounds of the type of the trinitrito triammine cobalt, that is, of the general formula $MX_3(NH_3)_3$ have the property of combining with more ammonia molecules still. Thus there are compounds of the types $MX_3(NH_3)_4$, $MX_3(NH_3)_5$, and $MX_3(NH_3)_6$. The addition of ammonia gives rise to a peculiar change in the function of the acid radicals, because for every additional NH_3-molecule that is taken on, one of the acid radicals enters the ionizable condition. If we compare the molecular conductivities in $\frac{1}{512}$ or $\frac{1}{500}$ normal solution at 250°, to wit:

	$Co(NH_3)_6X_3$	$Co(NH_3)_5X_3$	$Co(NH_3)_4X_3$	$Co(NH_3)_3X_3$
α	402	245	117	7

with those of the salts:

	Na_3PO_4	$MgCl_2$	$NaCl$	——
α	370	249	125	

we find that the first of the above complex salts must be a quaternary, the second a ternary, the third a binary, electrolyte, and the fourth a non-electrolyte.

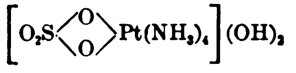
The chemical properties of these compounds accord perfectly with this theory. In the compound, $Co(NH_3)_4Cl_3$, formerly called "praseo-cobalt chloride," only one chlorine can be directly precipitated by silver nitrate; in $Co(NH_3)_5Cl_3$ two can be so precipitated, while in $Co(NH_3)_6Cl_3$, hexammine cobaltic chloride, all three chlorine atoms appear to be ionized in aqueous solution, since all three react at once with a silver salt solution. This is explained on the assumption that the added ammonia molecules displace the acid radicals from their immediate connection with the metal atom and themselves enter into this direct union with the metal. In order to distinguish the ammonia molecules which are linked up in this way **Werner** applies to them the term *ammine* and devises the following formulæ and names to express the constitution of the above-named compounds:

$M(NH_3)_3X_3$ Tri-acido triammine compounds $[M(NH_3)_3X_3]$,
$M(NH_3)_4X_3$ Di-acido tetrammine salts $[M(NH_3)_4X_2]X$,
$M(NH_3)_5X_3$ Acido pentammine saltt $[M(NH_3)_5X]X_2$,
$M(NH_3)_6X_3$ Hexammine salts $[M(NH_3)_6]X_3$,

the atoms or groups within brackets being regarded as in direct union with the metal atom. The ionizable groups X outside of the brackets are in indirect union with the complex and, according to WERNER, are not joined to a definite elemental atom.

If we compare the composition of the various metal-ammonias, we find that the formation of complexes is not without its limitations, but that after the addition of a definite number of NH_3-molecules it comes to an end. Particularly sharp is the limit in respect to the number of groups which can unite directly with an atom serving as the center of a complex radical. It is a striking fact that this limit is the same for a good many elements and is commonly six (6). It seems most likely that this limiting number is characteristic of the elemental atom and of considerable importance. WERNER calls it the **coordination number** and defines it as the maximum number of individual groups that can be directly united to an elemental atom. As already stated, the coordination number for most elements is 6; for a few elements, boron, carbon, and nitrogen, it is 4.

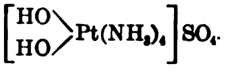
319. The constitution deduced for the metal-ammonia compounds enables us to explain in a very simple way a series of isomerism phenomena that are characteristic of these compounds. Two isomeric compounds are known of the formula $Pt(NH_3)_4 \cdot SO_4(OH)_2$. One behaves as a strong base, absorbing carbon dioxide from the air like caustic alkalies and precipitating metallic oxides from their salts, but gives no reaction of the sulphate ion in aqueous solution, e.g., no precipitate of barium sulphate with barium salts. The second compound is a perfectly neutral salt and acts as a normal sulphate, giving a barium sulphate precipitate at once with barium salts. We conclude from these reactions that the first compound gives only OH-ions; the second, on the contrary, only SO_4-ions. The cause of the isomerism is explained in the following coordination formulæ:



$$\left[O_2S\begin{matrix}\diagup O \diagdown \\ \diagdown O \diagup\end{matrix}Pt(NH_3)_4\right](OH)_2$$

Sulphato tetrammine plato hydroxide

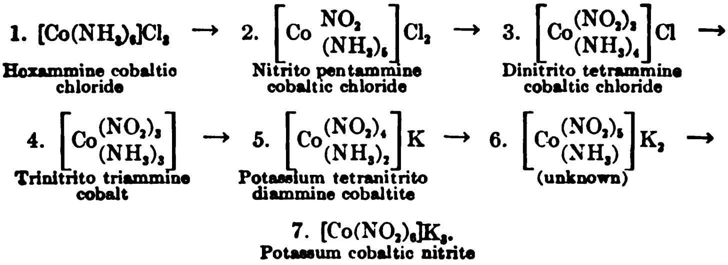
and



$$\left[\begin{matrix}HO\diagdown \\ HO\diagup\end{matrix}Pt(NH_3)_4\right]SO_4.$$

Dihydroxylo tetrammine plato sulphate

The researches on metal-ammonia compounds have been of great assistance in clearing up the structure of many complex salts, since the latter can be prepared by the gradual replacement of NH_3-groups by other molecules. An illuminating example of this is potassium cobaltic nitrite (§ 310), whose relation to hexammine cobaltic chloride is shown by the following series of ammonia compounds:



1. $[Co(NH_3)_6]Cl_3$ → 2. $\left[Co\begin{matrix}NO_2\\(NH_3)_5\end{matrix}\right]Cl_2$ → 3. $\left[Co\begin{matrix}(NO_2)_2\\(NH_3)_4\end{matrix}\right]Cl$ →

Hexammine cobaltic chloride — Nitrito pentammine cobaltic chloride — Dinitrito tetrammine cobaltic chloride

4. $\left[Co\begin{matrix}(NO_2)_3\\(NH_3)_3\end{matrix}\right]$ → 5. $\left[Co\begin{matrix}(NO_2)_4\\(NH_3)_2\end{matrix}\right]K$ → 6. $\left[Co\begin{matrix}(NO_2)_5\\(NH_3)\end{matrix}\right]K_2$ →

Trinitrito triammine cobalt — Potassium tetranitrito diammine cobaltite — (unknown)

7. $[Co(NO_2)_6]K_3$.

Potassium cobaltic nitrite

In all these compounds there is no ionizable NO_2-radical. The existence of such transition series clearly brings out the constitutional relationships which must exist between the metal-ammonias and the complex salts. The formulæ for these are so constructed that the groups which do not respond to analytical tests, as well as the NH_3-molecules displaced by them, are in direct union with the central metal atom.

The progressive substitution of NH_3 by a negative group or element results in the gradual decrease of the valence of the cation. While this is three in No. 1, it has become zero in No. 4, i.e., the molecule has become a non-conductor. If the substitution is carried further, as in Nos. 5, 6, and 7, the complex in brackets assumes the anion rôle and its negative charge increases from one to three. If the molecular conductivity for a given concentration is plotted on the ordinate axis in a diagram, we obtain for the series of compounds a curve, as is shown in Fig. 79. Numerous analogous transitions of metal-ammonia compounds to complex salts have been discovered, e.g.:

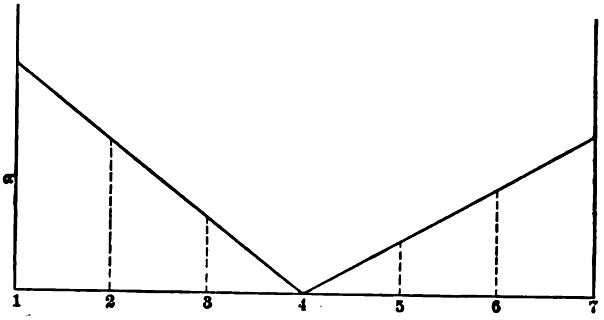
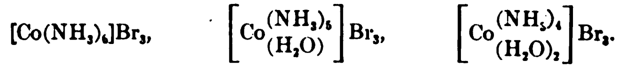


Fig. 79.

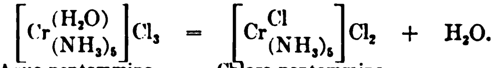
$$[Pt(NH_3)_6]Cl_4 \rightleftarrows [PtCl_6]K_2; \qquad [Pt(NH_3)_4]Cl_2 \rightleftarrows [PtCl_4]K_2; \text{ etc.}$$

Furthermore, relationships have been found to exist between metal-ammonias and *hydrates*. It is a significant fact that for a large number of salts of metals which give hexammine salts with ammonia, hydrates with six molecules of water predominate. This is the case with the salts of cobalt, chromium, nickel, etc. Moreover, **JÖRGENSEN** observed that compounds are derived from the hexammine salts by the exchange of one or two NH_3-molecules for water, which compounds correspond in behavior to the hexammine salts. This follows from the fact that the molecular conductivity in aqueous solution is but little affected by this exchange, e.g.:



$$\begin{array}{ccc} [\mathrm{Co(NH_3)_6}]\mathrm{Br_3}, & \left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_5}}{\mathrm{(H_2O)}}\right]\mathrm{Br_3}, & \left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_4}}{\mathrm{(H_2O)_2}}\right]\mathrm{Br_3}. \\ \alpha \quad 402 & 390 & 380 \end{array}$$

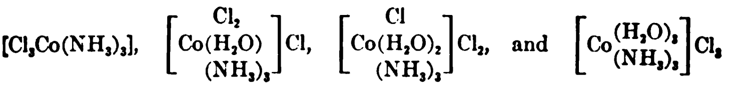
It is also confirmed by the fact that with the removal of each water molecule an acid radical loses its ionizing property, just as was the case for the removal of each ammonia molecule from the hexammine salts:



$$\left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{(H_2O)}}{\mathrm{(NH_3)_5}}\right]\mathrm{Cl_3} = \left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{(NH_3)_5}}\right]\mathrm{Cl_2} + \mathrm{H_2O}.$$

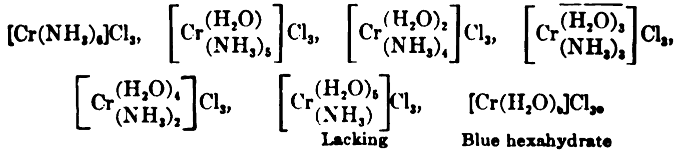
Aquo pentammine chromic chloride   Chloro pentammine chromic chloride

The addition of water has the opposite effect. The trichloro triammine cobalt, for example, is known to form hydrates with 1, 2, and 3 mols. water. Since all of the three chlorine atoms in the trihydrate have an ionizing character, while in the diyhdrate only two have this property, in the monohydrate one and in the anhydrous compound none, we are justified in ascribing to them in the following constitution:



$$[\mathrm{Cl_3Co(NH_3)_3}], \quad \left[\begin{matrix}\mathrm{Cl_2}\\ \mathrm{Co(H_2O)}\\ \mathrm{(NH_3)_3}\end{matrix}\right]\mathrm{Cl}, \quad \left[\begin{matrix}\mathrm{Cl}\\ \mathrm{Co(H_2O)_2}\\ \mathrm{(NH_3)_3}\end{matrix}\right]\mathrm{Cl_2}, \text{ and } \left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{(H_2O)_3}}{\mathrm{(NH_3)_3}}\right]\mathrm{Cl_3}$$

A nearly complete transition series from a metal-ammonia to a hydrate (hydrous salt) is to be found in the case of chromium:



$$[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}, \quad \left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{(H_2O)}}{\mathrm{(NH_3)_5}}\right]\mathrm{Cl_3}, \quad \left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{(H_2O)_2}}{\mathrm{(NH_3)_4}}\right]\mathrm{Cl_3}, \quad \left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{(H_2O)_3}}{\mathrm{(NH_3)_3}}\right]\mathrm{Cl_3},$$

$$\left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{(H_2O)_4}}{\mathrm{(NH_3)_2}}\right]\mathrm{Cl_3}, \quad \left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{(H_2O)_5}}{\mathrm{(NH_3)}}\right]\mathrm{Cl_3}, \quad [\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}.$$

Lacking   Blue hexahydrate

All these compounds contain three chlorine atoms in ionizable linkage; accordingly silver nitrate at once precipitates all the chlorine as silver chloride, even from freshly prepared solutions of the salts. The function of water in these compounds corresponds perfectly to that of the water in the aquo-salts of the cobalt ammonias, i.e., with the release of each water molecule a chlorine atom sacrifices its ionizing ability.

Two hexahydrates of chromic chloride, $CrCl_3 \cdot 6H_2O$, are known, one blue and the other green. The blue one contains three ionizable Cl-atoms, and according to its general behavior should be regarded as $[Cr(OH_2)_6]Cl_3$, hexaquo chromic chloride. Upon the loss of two water molecules it goes over into dichloro tetraquo chromic chloride $[Cl_2Cr(OH_2)_4]Cl$, which contains but one ionizable Cl-atom.

If this dichloro tetraquo chloride is crystallized out of water, it adds on two molecules of the water and goes over into the green hydrate, $[Cl_2Cr(OH_2)_4]Cl + 2H_2O$, which is thus isomeric with the blue hydrate. The green hydrate, moreover, contains only one chlorine atom that can be precipitated directly with silver nitrate. It should also be mentioned that the green hydrate can be transformed into the blue one and the water molecules, that condition the isomerism, shifted. Since the isomerism must depend on the difference in the manner of attachment of the water, **Werner** has called it **hydrate isomerism.**

Various cases of isomerism that are met with in the metal-ammonia compounds are best explained as cases of **stereo isomerism.** Two series of compounds are known of the general formula, $Pt_{X_4}^{(NH_3)_2}$; they are called **platin diammine compounds and have been known since 1870.** Later investigations have shown that this kind of isomerism occurs only with compounds of the type $M_{B_4}^{A_2}$. The assumption can therefore be made that the six groups are arranged at the apexes of an octahedron around the central

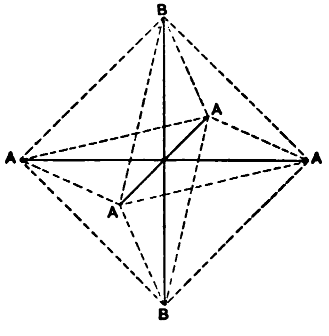


Fig. 80.

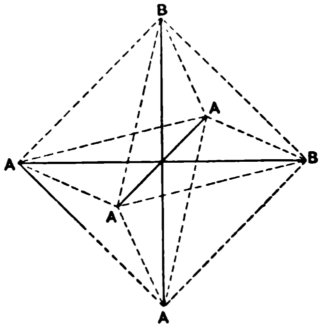
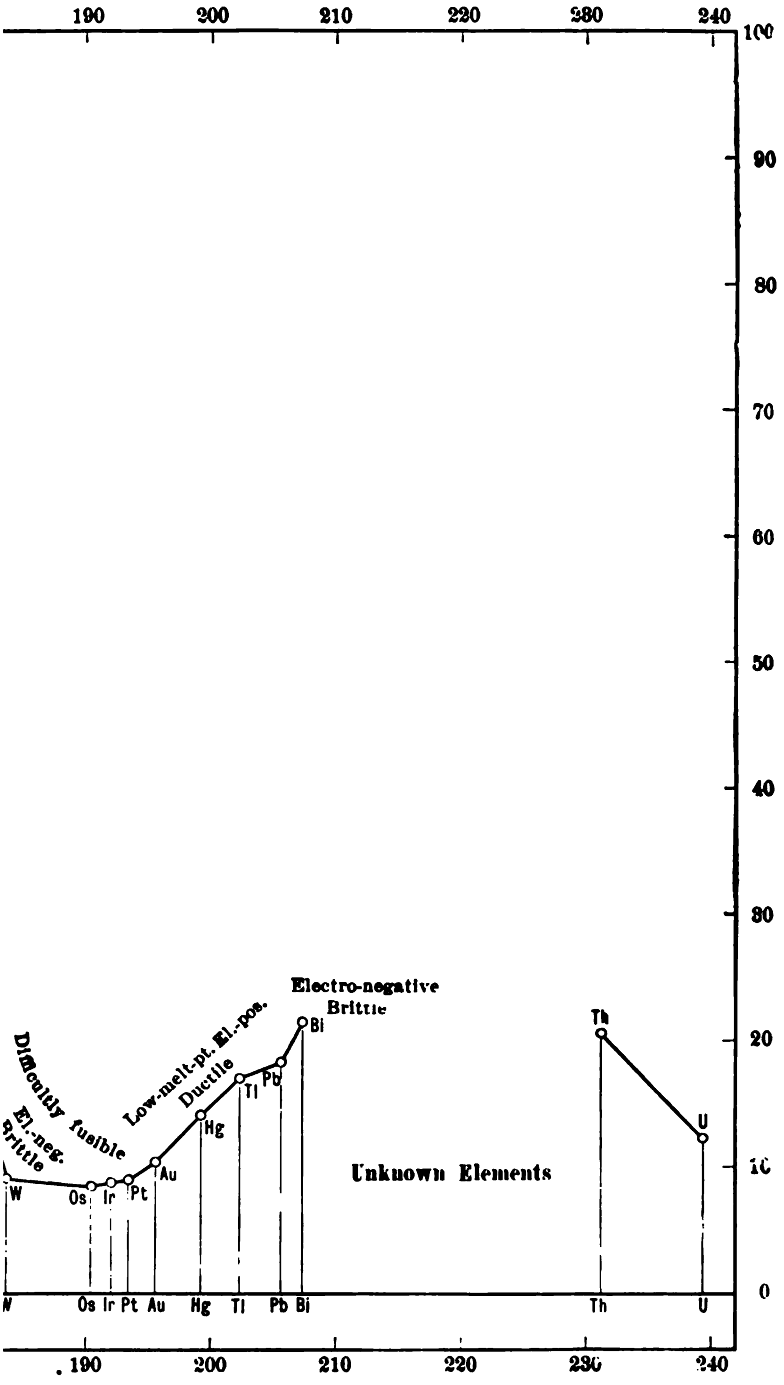


Fig. 81.

atom. Only with the type above described are two isomers possible, as the accompanying figures (Figs. 80 and 81) show. Compounds of the $M^{A_5}_{B}$ type cannot, therefore, have isomers and, as a matter of fact, no one has yet been able to prepare such isomers.

WERNER has also discovered metal-ammonias of more than one nucleus, i.e., where the molecules contain several metal atoms joined to one another in such a way as to undergo no separation either by ionization or by spontaneous hydrolysis; but we cannot dwell longer upon the subject here.

PLATE I.


190
200
210
220
230
240
100
90
80
70
60
50
40
30
20
10
0
Difficultly fusible
El.-neg.
Brittle
Low-melt-pt. El.-pos.
Ductile
Electro-negative
Brittle
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
Unknown Elements
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
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Aluminium	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.0
Argon	A	39.9	Nickel	Ni	58.68
Arsenic	As	74.96	Niobium	Nb	93.5
Barium	Ba	137.37	Nitrogen	N	14.01
Beryllium	Be	9.1	Osmium	Os	190.9
Bismuth	Bi	208.0	Oxygen	O	16.00
Boron	B	11.0	Palladium	Pd	106.7
Bromine	Br	79.92	Phosphorus	P	31.0
Cadmium	Cd	112.40	Platinum	Pt	195.0
Caesium	Cs	132.81	Potassium	K	39.10
Calcium	Ca	40.09	Praseodymium	Pr	140.6
Carbon	C	12.00	Radium	Ra	226.4
Cerium	Ce	140.25	Rhodium	Rh	102.9
Chlorine	Cl	35.46	Rubidium	Rb	85.45
Chromium	Cr	52.0	Ruthenium	Ru	101.7
Cobalt	Co	58.97	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.4	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.62
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.0
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.0	Terbium	Tb	159.2
Hydrogen	H	1.008	Thallium	Tl	204.0
Indium	In	114.8	Thorium	Th	232.42
Iodine	I	126.92	Thulium	Tm	168.5
Iridium	Ir	193.1	Tin	Sn	119.0
Iron	Fe	55.85	Titanium	Ti	48.1
Krypton	Kr	83.0	Tungsten	W	184.0
Lanthanum	La	139.0	Uranium	U	238.5
Lead	Pb	207.10	Vanadium	V	51.2
Lithium	Li	7.00	Xenon	Xe	130.7
Lutecium	Lu	174.0	Ytterbium (Neoytterbium)	Yb	172.0
Magnesium	Mg	24.32			
Manganese	Mn	54.93	Yttrium	Y	89.0
Mercury	Hg	200.0	Zinc	Zn	65.37
Molybdenum	Mo	96.0	Zirconium	Zr	90.6